ANALYTICAL STUDIES OF ORGANIC AND INORGANIC POLLUTANTS

SUMMARY

THESIS SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

IN

Applied Chemistry

BY

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DEPARTMENT OF APPLIED CHEMISTRY
Z. H. COLLEGE OF ENGINEERING & TECHNOLOGY
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LIST OF PUBLICATIONS

1. Twenty-two years report on the thin-layer chromatography of inorganic mixtures : Observations and future prospects (Review), Ali Mohammad, Mohammad Ajmal, Shahana Anwar and **Eram Iraqi**, *Journal of Planar Chromatography-Mod. TLC* (Hungary), 9 (1996) 318-360.

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SUMMARY

The work summarized in this thesis involves the use of thin layer chromatography (TLC) as an analytical tool for identification and separation of some organic (aromatic amines and phenols) and inorganic (heavy metal cations) pollutants. TLC coupled with spectrophotometry has been used for quantitative determination of cobalt and uranium after their separation from interfering metal ions. In quest of an inexpensive methodology for the identification and separation of pollutants, several chromatographic systems involving new and cost effective layer materials and novel eluent solvents have been developed. The results presented in the thesis contribute substantially to the advancement of normal-phase and reversed-phase TLC procedures. The complete work performed has been summarized in the form of seven chapters, discussed briefly as:

Chapter I an introductory part, provides a general idea about the environmental pollution, elements of pollution, classification of pollutants, sources of some organic and inorganic pollutants and their effects. Besides, a detailed description of TLC along with complete literature survey (1991-1997) on its application to inorganic ions, aromatic amines and phenols has been provided in this chapter.

Chapter II deals with the development of a new layer material consisting of stannic arsenate gel mixed with silica gel G for normal phase and reversed-phase TLC of metal ions. The analytical potential of tributylphosphate (TBP) as impregnant as well as eluent has been explored. Separation of coexisting nickel, cobalt and iron ions from acidic and ammoniacal solutions on stannic arsenate-silica gel G (10:1, w/w) mixed sorbent layers impregnated with 0.2M TBP in acetone and 1.0M KSCN-5.0M HCl 1.0 M NaCl (8:1:1) mobile phase has been

obtained. Effect of pH of sample, loading amount of analyte, presence of amines, phenols and anions on the separation of Ni^{2+} from Co^{2+} has been carried out to optimize the experimental conditions. The identification and separation of Ni^{2+} , Co^{2+} and Fe^{3+} from distilled water, sea water, industrial waste water, high speed steel sample and geological samples have been achieved. The proposed method is sensitive for the detection of Ni^{2+} (2.47 μg), Co^{2+} (2.02 μg) and Fe^{3+} (1.72μg) as their chloride salts.

Chapter III illustrates the use of thin layer chromatography in combination with spectrophotometry for the separation and determination of cobalt after its separation from nickel in aqueous samples. A chromatographic system consisting of a mixture containing stannic arsenate gel and silica gel G in 10:1, w/w ratio as stationary phase and 1M aqueous potassium thiocyanate as mobile phase has been used to separate cobalt from nickel. Effects of acidity and alkalinity of sample solution on the separation of Co^{2+} from Ni^{2+} were examined. Microgram separation of cobalt from variable amounts of nickel has been achieved after pre-concentration of metal ions from aqueous solutions by, sulphide precipitation. Determination of cobalt after TLC separation provides a recovery of 92% and the Beer's law is obeyed in the range 49-345 μg of Co^{2+} per 25 ml. The well resolved spots with ΔR_F values were obtained for Co^{2+} and Ni^{2+} .

Chapter IV encapsulates the migration behaviour of heavy metal cations on cellulose layers using aqueous micellar, hydro-organic and water-organic-surfactant mobile phases. Anionic, cationic and non-ionic surfactants were used as micelles. A non-ionic surfactant, Brij-35 capable of forming charged complexes with some metal ions was identified as the best surfactant and it was used as mobile phase over 0.001-5% concentration range. The effect of the presence of organic additives (DMSO, DMF, acetone, methanol etc.) on the mobility of metal ions

was also examined. Acetone with wider separation possibilities was found the most effective additive at 10% concentration with 3% Brij. Quantitative determination of UO_2^{2+} by spectrophotometry after TLC separation from Fe^{3+} and Hg^{2+} was performed and a maximum recovery of 93% was obtained. The developed TLC method is rapid as development time of 2 min is only required for 5cm ascent.

Chapter V describes the synthesis of two inorganic ion-exchangers i.e. stannic arsenosilicate and zirconium tungstophosphate as well as the formation of mixed layers prepared from mixture of silica gel and inorganic ion-exhangers. These new layer materials include the combined effect of ion-exchange properties of synthetic inorganic ion-exchange gels with adsorptive properties of silica gel. The first part of this chapter describes the use of silica gel-supported stannic arsenosilicate gel as stationary phase for detection and selective separation of certain heavy metals. Mixed sorbent layer comprising of silica gel G and stannic arsenosilicate gel in 1:1 w/w ratio and impregnated with 10% tributylamine (TBA) developed in 1M formic acid - 1M sodium formate 4:1 v/v, mobile phases was found to be the best chromatographic system for maximum separation possibilities of heavy metals. TBA as impregnant proved better as compared to its use as mobile phase. The loading effect and the limit of detection of metal ions were investigated.

In the second part of this chapter an attempt is made to examine the use of zirconium tungstophosphate inorganic ion-exhanger gel mixed with silica gel G in reversed-phase TLC of metal ions. This mixed layer material was used after impregnation with tributylphosphate (TBP) at different concentration levels to separate metal ions using HCl or formic acid containing solvent systems as eluents. Efforts were also made to explore the possible use of crown ethers as impregnants or as eluents in inorganic TLC. The variation of R_F values of metal ions on TBP impregnated stationary phase (silica gel G - zirconium tungstophosphate 1:1) led to some important separations.

Thus, these newly developed sorbent phases, can be utilized as inexpensive and highly selective layer material for the identification, detection and separation of certain heavy metals.

Chapter VI presents the use of water-in-oil (w/o) microemulsions consisting of surfactant (sodium dodecylsulphate or N-cetyl-N, N, N-trimethyl ammonium bromide), water, heptane or hexane and a cosurfactant (1-pentanol or butanol) as mobile phase in combination with alumina microcrystalline cellulose, silica gel G, silica gel H and kieselguhr thin layers to study the retention efficiency of amines. The separation of amines from their ternary and binary mixtures are achieved. Thin layers of alumina as stationary phase and SDS-water-heptane-n-pentanol microemulsion as mobile phase was identified as the best chromatographic system for the analysis of aromatic amines. The effect of heavy metals anions and phenols on the separation efficiency of diphenylamine-p-chloroaniline-p-nitroaniline have also been examined. The effect of electrolyte in microemulsion solution on the mobility of amines is investigated. o-and p-isomers move faster compared to m-isomers of aniline. The limits of identification and dilution are reported for amines.

Chapter VII summarizes the results of thin layer chromatographic behaviour of some phenols and amines chromatographed on layers of unimpregnated and impregnated chicken egg-shell powder. Various organic solvents and aqueous salt solutions of ammonium and potassium were used as mobile phases. The mobility of amines and phenols was found to depend on the polarity of the solvent used and the nature of the impregnant. The selectivity of chicken egg-shell layers towards organic compounds was investigated under the influence of different concentrations of copper sulphate, tributylamine and tributylphosphate. Several important separations including the separation of indole from carbazole and diphenylamine has been experimentally realized.

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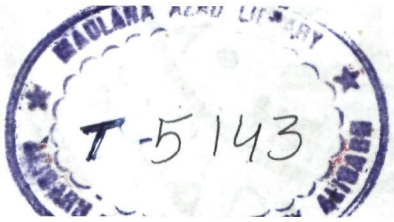
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To My Parents

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CERTIFICATE

Certified that the work incorporated in this thesis entitled "Analytical Studies of Organic and Inorganic Pollutants" is the original contribution of Ms. Eram Iraqi, carried out under my supervision and is suitable for submission for the award of Ph. D. degree in Applied Chemistry.

Ali. Mohammad

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Supervisor

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CHAPTER I

GENERAL INTRODUCTION

1.1 INTRODUCTION

Analytical Chemistry is one of the most important branches of chemistry. It is being used for the detection and determination of traces of pollutants in air, water and soil environments. Owing to the great importance of pollution in modern life, the environmental chemistry is becoming more and more relevant. By environment we mean not only our immediate surrounding but also a variety of issues connected with human activity, productivity, basic living and its impact on natural resources such as land, water, atmosphere, forests, habitat, health, energy, resources, wild life etc. In relation to man, the environment constitutes of air, land, water, flora and fauna because these elements regulate the man's life.

1.2 POLLUTION AND POLLUTANTS

The addition to the environment of any substance or energy form at a rate that results in higher than natural concentrations of that substance or energy form is termed as *"Pollution"*. The more acceptable definition of pollution is given by Holdgate which states that *"pollution is the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living sources and ecological systems, damage to structures or interference with legitimate uses of the environment"*. Pollutant is a substance present in nature, in greater than natural abundance due to human activity, which ultimately has a detrimental effect on the environment and therefrom on living organisms and mankind.

Some substances such as radioactive dusts and certain pesticides (e.g. DDT), can be relatively long lasting and can disperse readily to the point that they become virtually world wide in distribution. Such pollutants which include many chlorinated hydrocarbon insecticides and several toxic mercury compounds, may enter biological food chains by

becoming concentrated in the bodies of microorganisms (algae and protozoans) and move upward as successively larger organisms prey upon smaller ones.

Pollutants are commonly classified according to the part of the environment primarily affected by them, either the air, water or land. Many serious pollutants are closely and fundamentally bound to vital agricultural or industrial systems or products. Abatement of a given pollutant may involve the total redesign of an industry or its' product. Subgrouping of pollutants depend on characteristics of the pollutants themselves; chemical, physical, thermal and others. Pollutants generally affecting the environment may be broadly categorized as inorganic and organic pollutants.

Inorganic pollutants consist of inorganic salts, mineral acids, finely divided metals, metalloid or metal compounds, trace elements and organometallic compounds. Organic pollutants include oxygen demanding wastes, disease causing agents, plant nutrients, sewage, synthetic organic compounds like alcohol, ketones, aldehydes, amines, phenols, organic acids and others.

Many inorganic compounds, especially metal ions, are playing a double role in the physiology of organism. Some are indispensable for normal life while most of them are toxic at elevated concentrations i.e. they adversely affect the activity and well being of living organisms. Recent years have brought an increasing concern for the potential toxic effects of metal ions and other inorganic compounds, which constitute part of the products and by-products of our technologies. This is especially true for heavy metals because it is not ametioratd by natural phenomena of biochemical decomposition. High concentration of heavy metals in surface water is generally associated with industrial discharges (1,2). Metals containing industrial waste constitute a major source of metallic pollution of the hydrosphere. The tremendous increase in the

use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. The important sources of metal pollution involves domestic sewage (3), geological weathering, mining effluents (4,5), atmospheric sources (6), and urban storm water run off (7,8).

Similarly all organic compounds are suspected to be carcinogenic. The presence of synthetic organic chemicals in water imparts objectionable smell and offensive taste, odour to fish and aquatic plants even if present in low concentrations. Accumulation of these chemicals in soil and their subsequent mobilization into the plants have posed a serious concern (9). Organic particulate matter originates from wide variety of sources such as emission from vegetation and automobiles, combustion of fuels etc. Polycyclic aromatic hydrocarbons (PAH) in organic particulate matter are known to have carcinogenic effect. Naturally occurring chelating agents such as humic acids and aminoacids exist in natural water and soil. The properties of water are generally influenced by the humic substances, both soluble and insoluble due to their acid-base, adsorptive and complexing properties. The soluble fulvic acid has an effect on the properties of water, while the insoluble humin and humic acids affect quality through exchanges of cations, organic materials etc., with water.

The first international conference on Earth held in Rio in 1992 may be considered to be the start of awareness for environmental pollution. Environmental education is important to enlighten the public regarding the harmful effects of pollution and its remedial measures so that a cleaner environment may be obtained. History of civilization reveals that water supply and civilization are almost synonymous. Millions of people all over the world particularly in the developing countries are losing their lives every year from waste borne diseases. The quality of water is of vital concern for mankind since it is directly linked with human welfare.

Some important organic and inorganic pollutants present in water, their sources and effects are listed in Table 1.1.

Table 1.1 : Some Important Organic and Inorganic Pollutants in Water and Their Significance.

Pollutant	Source	Effect/Significance
Phenols	Cock-oven, coal distillation plants and industrial waste waters	Toxic and imparts objectionable taste in chlroinated drinking water
Oil	Oil spills from cargo oil tankers/pipelines on the seas, losses during off shore exploration and production of oil	Decreases dissolved oxygen in water and causes damage to water birds, coastal plants and animals
Pesticides	Extensive use in agriculture and forest areas	Adverse effect on the biota and physical environment
Naphthyl amines	Dye and colour film manufacture	Bladder cancer
N-ethyl-N-nitroso -N-butylamine	Gasoline, lubricant additive and insecticides etc.	Carcinogenic
Methyl-chloro-methyl	Ion-exchange resin manufacture	Lung Cancer

Arsenic	Mining bye-product pesticides, chemical waste, pharmaceutical and paper industry	Acute poisoning results, severe gastro intestinal irritation with attendant cramps and diarrhoea, nervous disorder
Cadmium	Industrial discharge, mining waste, metal plating and water pipes	Replaces zinc biochemically causes high blood pressure, kidney damage, destruction of testicular tissues and red blood cells
Chromium	Metal plating, paint alloy and glass industry, electroplating effluents and tannery waste	Cr(VI) is very toxic, causes ulceration and carcinoma
Copper	Metal plating industry, domestic waste, mining and mineral leaching	Essential tissue element but toxic to plants and algae at moderate levels. Excess intake is injurious to health
Cobalt	Magnet making concerns and industrial discharge	Essential at moderate level but at higher concentration causes coronary failure, thyroid, dysfunction due to impaired accumulation of iodine

Iron	Water flowing through Basaltic rock region and industrial effluents	Essential for many biological activities. Causes homochromatosis, tension in gastrointestinal tract, shock and liver damage
Lead	Autoexhaust emission as ethyl lead and industry (glass, paint, mining, plumbing, coal, gasoline)	Toxic, deactivates or destroys sulphur containing proteins and enzymes, damages DNA, RNA, brain and central nervous system function. Inhibits the formation of haemoglobin
Manganese	Mining, industrial waste, acid mine drainage, alloy industry, dry cell battery factories and glass industry	Relatively non toxic to animals and irreversible damage to the CNS and brain (ataxia)
Mercury	Mining industrial waste, pesticides and coal (chloralkali industry)	Highly toxic as methyl mercury ion $HgCH_3^+$. Toxic even at a concentration of 0.03 ppm in drinking water. Hg activates sulphur containing enzymes with active -SH group. Affects brain cells and central nervous system

Molybdenum	Coal fired power plants, industrial wastes and natural sources	Toxic to animals, essential for plants. Hard metal lung disease
Nickel	Hydrogenation of oil industry and paint factories	$Ni(CO)_4$ is the most toxic. Causes lung cancer, gastro-intestinal disorder and degeneration of heart and tissues, giddiness, headache, nausea, vomitting
Selenium	Glass and photocell industry and natural sources	Essential at low level, causes cancer, deformed nails and hair
Vanadium	Furnace oil boilers, milling operations in steel industry, heat exhangers fired with reduced oil causes pollution	Reduces cystain contents of hair and nails. Cancer, reduced growth, adverse effect on eyes and respiratory tract
Zinc	Galvanization industry, alloy industry, metal plating and plumbing	Essential in many metallo enzymes toxic to plants at higher levels. Inhaled Zn fumes causes metal fume fever, vomiting chills etc.

The properties and composition of substances containing elements are quite varied. Analytical methods are widely used to check the composition of raw materials to control various processes. It is impossible to obtain high purity materials unless production processes are provided with adequate analytical control at each important stage. The importance of having a chemical analysis lies in the fact that the presence of any impurity in a substance plays a vital role in chemical as well as physical properties of the materials. Consequently, the need of analytical chemistry is increasing as the newer problems are arising owing to different demands of the modern world. By analytical chemistry we mean the development of new methods suited for the requirements of the mankind. The classical methods have to be modified according to the needs of the situation and new methods have to be developed for solving the problems of current interest e.g. purification of environment, analysis of ores, recovery of precious metals from the spent fuel, solar energy utilization etc.

Chemical analysis establishes the qualitative and quantitative composition of materials. The constituents to be detected or determined are elements, radicals, functional groups, compounds or phases. A qualitative analysis deals with the methods used for the determination of the nature of the constituents of a substrate whereas the quantitative analysis is concerned with the methods dealing with the determination of actual amount of a given species present in a sample. The methods involved in chemical analysis may be instrumental and non-instrumental (classical). Instrumental methods involving the application of the principles of physical chemistry and physics to the chemical analysis are usually faster and more sensitive, whereas non-instrumental methods which form the basis of standardization of the instruments are considered more accurate. Prior to many qualitative and quantitative analyses, it is necessary to remove interfering substances. Separations are always a

must when we consider the purification and isolation of substances.

Modern research has imposed very exacting requirements on separation procedures. Consider only a few requirements : the reduction of impurities in germanium, the separation of the rare earth metals, resolution of complex mixtures of aminoacids and the separation of the various isotopes of an element and the various isomers of a complicated compound. These are fabulous accomplishments which emphasize the importance of separation techniques to modern technology. Other more challenging separation problems are constantly arising to take the place of those solved.

Adsorption, chromatography, ion-exchange, flotation, extraction, dialysis, etc. have now become as familiar tools in the hands of the researchers as the more conventional techniques of precipitation fractional crystallization and distillation. The objective researcher can no longer confine himself to a single method for resolution of a mixture. Indeed, the outstanding accomplishments of recent years have stressed the need for the successive application of different techniques that depend upon widely different chemical or physical properties of the sample molecules.

The combination of techniques and processes and selection of methods most applicable for a given system require a thorough knowledge of the practical limitations inherent in each method. The choice of separation tool is usually governed by the size of sample available, the simplicity and selectivity of the method, the degree of the resolution required and the general applicability of the procedure. The most general methods of separation are chromatography, ion-exchange and electrophoresis. These methods are fast, selective and sensitive and therefore they generally precede the quantitative analysis of organic and inorganic mixtures.

1.3 CHROMATOGRAPHY

Chromatography has been defined by Casidy(10) as *"A separation process applicable to essentially molecular mixtures which relies on distribution of the mixture between an essentially two dimensional or thin phase and one or more bulk phases which are brought into contact in a differential counter current manner."* It is interesting to note that, inspite of the general acceptance of the contributions of Tswett as being among the first to advocate adsorption in separation technology, this investigator was not the real discoverer of chromatography. The beginning of chromatography may be attributed to Runge (11) who published his work on dye separation on paper in 1855. However, the real start of chromatographic analysis should be credited to Goppelsroeder, who presented some of his work in 1861(12) and Schonbein, who described separation of substances adsorbed onto filter paper (13). In 1897, Day demonstrated the use of columns for separation of petroleum fractions (14). The 'rediscovery' of chromatography as it is now known dates from the reports of separations on column by Kahn and Lederer (15). Lederer separated carotenoids from egg yolk following Tswett's description of chromatography. The subject of chromatography may be divided and subdivided as shown in Fig. 1.1. Whereas the realization of a chromatographic experiment is simple, the mechanism of the chromatographic process is complex because a number of important chromatographic processes proceed spontaneously.

According to the physical arrangement chromatographic systems can be divided into planar and column. The planar arrangements are represented by systems of paper and thin layer chromatography. In planar chromatographic systems the solute components are generally not eluted from the chromatographic bed but rather detected directly in it, whereas, in column chromatography the solute components are gradually eluted with the mobile phase and detected in the effluent at the column outlet.

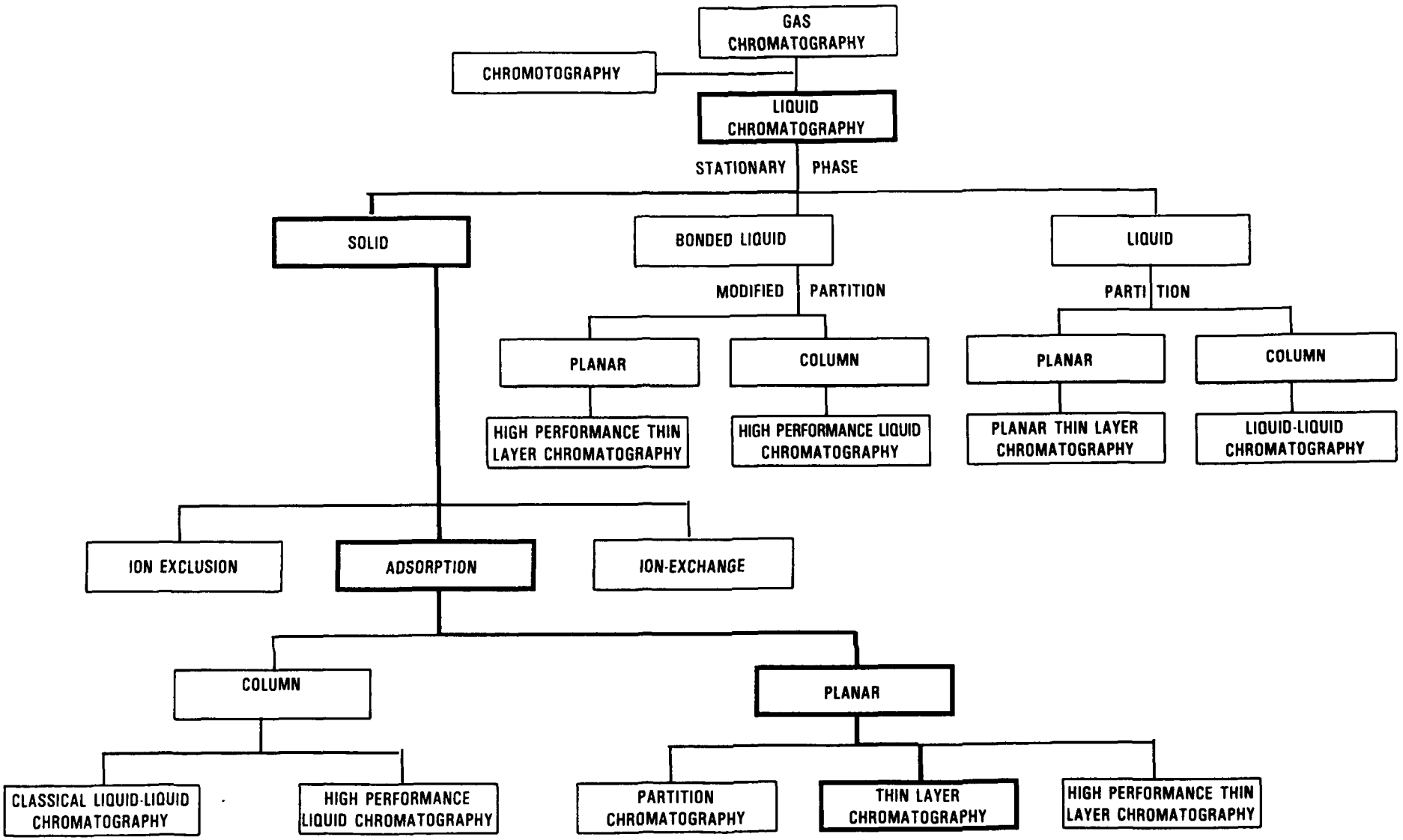

FIG. 1.1 : SCHEMATIC REPRESENTATION OF CHROMATOGRAPHIC TECHNIQUES

Since the work summarized in this thesis is based on thin layer chromatography, it is worthwhile to summarize the important features of this technique. The following paragraphs are devoted to outline the development and current state-of-art procedures of TLC as used to the analysis of inorganics, aromatic amines and phenols.

1.4 THIN LAYER CHROMATOGRAPHY

Thin layer chromatography (TLC) is a subdivision of liquid planar chromatography in which the mobile phase (a liquid) migrates through the stationary phase (thin layer of porous sorbent on a flat inert surface) by capillary action. The beginning of TLC can be attributed to the report of Beyerink (16) who separated sulfuric and hydrochloric acids as rings on a thin layer of gelatin followed by the separation of two enzymes from malt diastase by Wijsman (17). In 1938, two Russian workers, Izmailov and Schraiber (18) separated certain medicinal compounds on binder free horizontal thin layer of alumina spread on a glass plate. Since the development was carried out by placing solvent drops on the glass plate containing sample and sorbent, their, method was called "*Drop chromatography*". This method remained unnoticed for 10 years till two American Chemists, Meinhard and Hall (19) used aluminium oxide (adsorbent) plus celite (binder) as a layer on a microscope slide to separate Fe^{3+} from Zn^{2+} . They called this technique as "*Surface Chromatography*".

The real impetus for advancement of TLC started in 1951 with the work of Kirchner (20-22) and his associates. Since 1958, when Stahl (23, 24) introduced the term '*thin-layer chromatography*' and standardized procedures, materials and nomenclature, the effectiveness of this technique for separation was realized. After the pioneering work of J. Kirchner and E. Stahl, who published books on the subject, TLC became important for the separation of samples not amenable to the analysis

by gas chromatography (GC). The rapid growth of TLC was slowed down during 1970's with corresponding rise in popularity of high pressure liquid chromatography (HPLC) and ion chromatography (IC). However, recent improvements in TLC have removed many of its limitations.

Dallas et al. (25) reported the densitometry in TLC in mid 1960s. In 1968, a symposium on quantitative TLC was held in Great Britain leading to the publication of the first book on this topic. High performance TLC plates were produced commercially in the mid 1970s. As a result of improvements in practice and instrumentation in the late 1970s and early 1980s, high performance (HP) TLC, overpressured (OP) TLC, centrifugal layer chromatography (CLC), and reversed phase (RP) TLC were originated. These and other sister high performance and quantitative techniques cause a renaissance in the field of TLC.

HPTLC layers being thinner and made of more uniform particle size sorbents provide faster separations, reduced zone diffusion, lower detection limits, less solvent consumption and better separation efficiency. Comparisons of TLC and HPLC are described in publications by Fenimore and Devis (1981), Borman (1982), Maugh (1982), Coddins et al. (1983), Jork and Wimmer (1986), Geiss (1987) and J. Sherma (1991, 1993). The distinct advantages of TLC over HPLC e.g. low solvent consumption, low operational cost, easier sample preparation, more rapid throughput, greater detection possibilities and the use of disposable plates have been identified. TLC permits the simultaneous analysis of many samples in the same time period required for one HPLC analysis. On the other hand, the samples and the standards are analyzed by TLC under exactly the same conditions rather than serially as in HPLC. Typically, 18-36 samples can be run on a single HPTLC plate with development time 3-20 min over short migration distance of 2-7 cm. However, the influence of environmental conditions on the reproducibility of R_F values and poor separation efficiency have been major disadvantages of TLC compared with HPLC and GC. In his recent article

Sz. Nyiredy (1992) has compared various planar chromatography techniques.

TLC can be used for (i) qualitative analysis (to identify the presence or absence of a particular substance in a mixture), (ii) quantitative analysis (to determine precisely and accurately, the amount of a particular substance in a sample mixture) and (iii) preparative analysis (to purify and isolate a particular substance for subsequent use). All three cases require the common procedures of sample applications, chromatographic separation and sample component visualization. However, analytical TLC differs from preparative TLC in that volumes and/or weights of samples are applied to thicker layers in the latter case.

1.5 TLC PROCEDURE

TLC is an off-line process in which various steps as illustrated in Fig. 1.2 are carried out independently. The basic TLC procedure involves the spotting of sample mixture (5-10μL for conventional TLC and 1-2μL for HPTLC) at about 1.5-2 cm above the lower edge of the layer, drying the spot completely at room temperature or at an elevated temperature, development of plate usually by one-dimensional ascending technique in a closed chamber (cylindrical or rectangular) to a distance of 8-10 cm, withdrawing of TLC plate from developing chamber, removal of mobile phase from the layer by drying, detection of spots on TLC plate using suitable detection reagent/procedure, measurement of R_F values of resolved spots and quantitative determination of the separated analyte. The differential migration of components in a mixture results due to varying degrees of affinity of the components for the stationary and mobile phases.

Sample Preparation

The sample solution to be analyzed must be sufficiently concentrated to provide clear detection or/and be pure enough so that it can be separated as a discrete and compact spot or zone. For low concentration of analyte in a complex sample, preconcentration and cleanup procedures precede TLC.

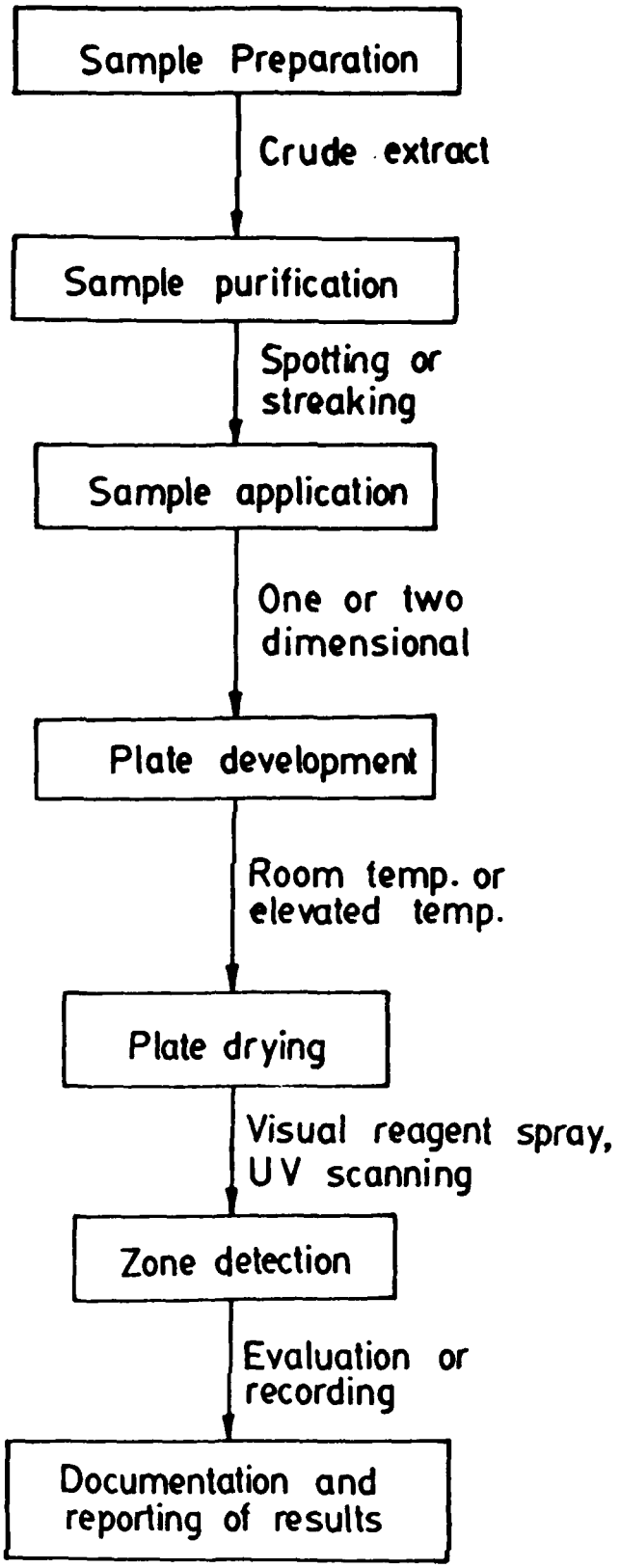

Fig. 1.2 Schematic Diagram Showing the Steps Involved in a TLC Process.

TLC Plate Preparation

The contemporary trend is of using commercially available precoated plates. The manual preparation of layers involves the coating of slurry of the adsorbent (silica gel, alumina, soil) on glass, aluminium or plastic sheet (20×20 or 20×10cm) with the help of TLC applicator. The thickness of dried layer for analytical purposes is kept to 0.1 - 0.3 mm. A binder (starch, gypsum, dextrin, polyvinyl alcohol) is usually added to the layer material to provide better adhesion, mechanical stability and durability. The addition of fluorescence indicator compound has been optional. Compared to conventional TLC, HPTLC layers are produced from sorbent of smaller and more uniform particle size (5-10μm instead of 10-20 μm).

1.6 SAMPLE APPLICATION

Definite volumes of samples are applied as spots or streaks using micropipette, microsyringe, melting point capillaries etc. A number of automatic spotters of varying design are available for sample application. The nano applicator (Nanomat) is an example of micrometer controlled syringe which has a dynamic volume range of 50-230nL. Another applicator (Linomat) allows sample application in narrow bands by a spray on technique. The application of sample as a streak or band provides more efficient separations because the efficiency (N) of the separation on a TLC plate depends on the diameter of the spot along the direction of development. Thus, the best efficiency is achieved with smallest diameter of the spot. Alternatively, the use of TLC plates with concentration zones converts the sample from original spot into a band or streak. These plates consist of a bottom layer (2-2.5cm) of a chromatographically inactive adsorbent (e.g. Kieselguhr) followed by the layer of an active adsorbent (silica or bonded silica). The advantages of sample application as streak and the use of TLC plates with concentration zones are illustrated in Fig. 1.3.

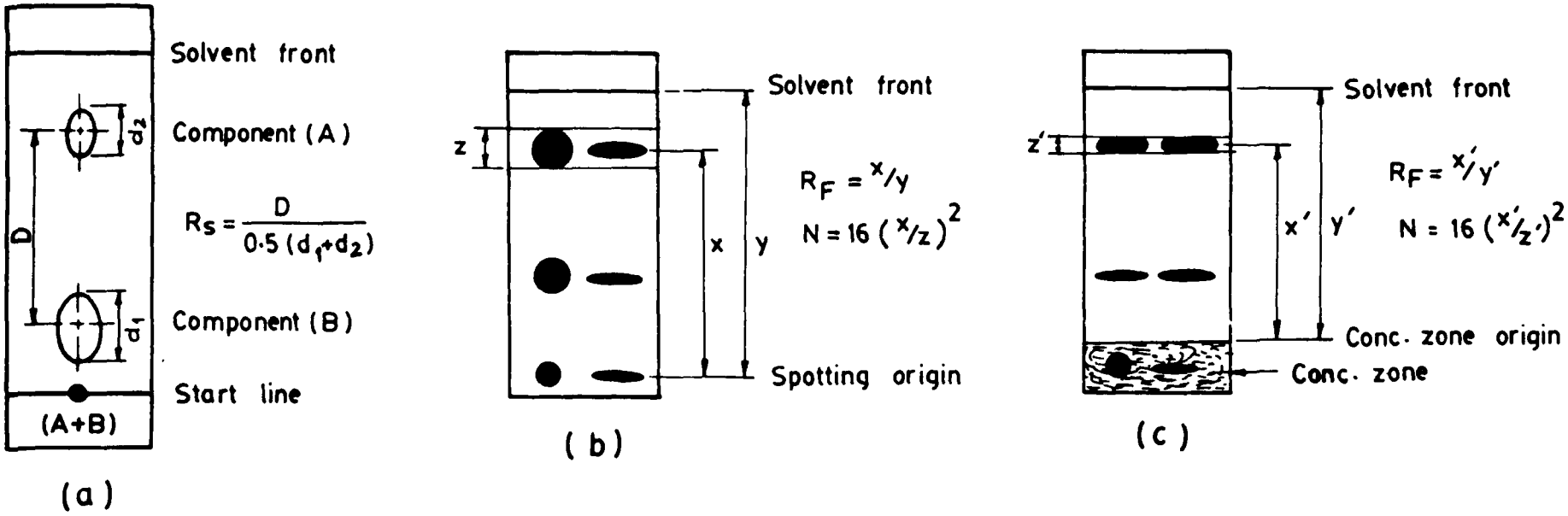

Fig. 1.3 Illustration of Resolution of a Two-Component Mixture on TLC Plate (Fig. 1.3a), Improved Efficiency Due to Streaking (Fig. 1.3b) and Utility of Concentration zone as a Promotor of Efficiency (Fig. 1.3c).

1.7 DEVELOPMENT TECHNIQUES

The process of migrating mobile phases through the stationary phase (or sorbent layer) to affect separation of sample substances is called development. One-dimensional ascending development technique has been the most commonly used mode of development. Other development techniques such as multiple, stepwise, circular, two-dimensional and reversed-phase partition development have also been used to limited extent. The migration distance for mobile phase has been kept to 10-12 cm for conventional TLC and 2-6cm for HPTLC.

1.8 CHROMATOGRAPHIC SYSTEMS

A combination of stationary and mobile phases constitutes chromatographic system. The proper selection of stationary and mobile phase conditions determines the extent of effective separation of components in a mixture.

Stationary Phase (Layer Sorbent)

Many layer materials have been used as stationary phase but silica gel, an amorphous and porous adsorbent has been the much favoured layer material followed by alumina and cellulose. Thin layers of silica gel G (gypsum binder) and S (starch binder) with or without "fluorescent indicator" have been used more frequently. Silica gel is slightly acidic in nature and the silanol groups (Si - OH) are capable to interact with solute molecules. On the other hand, alumina (aluminium oxide) is basic and more reactive than silica gel. Adsorption is the separation mechanism in both alumina and silica gel. Cellulose, an organic material is used as a sorbent to perform separations with increased sensitivity of detection and decreased development time compared to paper chromatography. The various layer materials used may be broadly classified as :

(a) Non-surface Modified Layers or Untreated Sorbents :

The sorbent phases used in the non-modified form include silica gel G, silica gel H, silica gel LS, acidic and neutral alumina, cellulose, polyacrylonitrile etc.

(b) Impregnated or Treated Sorbents (Organic and Inorganic Impregnants)

To broaden the range of selectivity of above mentioned layer materials, several workers attempted to use these materials after impregnation to a definite degree with buffers, metal ions, chelating agents or high molecular weight organic liquids. Some impregnated layers used include : silica gel impregnated with aqueous inorganic salt solutions; acid treated silica gel layers; silica gel impregnated with chlorobenzene, high molecular weight amines, tributylamine, tributylphosphate, chelating agents such as EDTA, ammonium rhodenate, and mixture of alizarin red S and aliquat 336; silica gel impregnated with surfactants, mono-(2-ethylhexyl) acid phosphate and p-toluitine and silufol impregnated with 5% paraffin oil.

(c) Chemically Modified or Bonded Sorbents (hydrophobic modified or reversed-phase and hydrophilic modified)

The impregnated layers suffer from the limitations such as (i) the impregnants are eluted to some extent by the mobile phases used and (ii) the stripping of liquid stationary phase from the support by incompatible mobile phases. To overcome these problems, chemically bonded layer materials of similar properties were developed for safer use as stationary phase. Some of the examples are : lipohilic C_{18} bonded silica gel phases, aminopropyl silica gel (NH_2), octadecyl silica gel (C_{18}) and surface-modified cellulose like ECTEOLA (a reaction product of epichlorohydrin triethanolamine and alkali cellulose).

(d) Inorganic Ion-Exchangers

Apart from silica and alumina, other inorganic ion-exchangers have also found use in TLC. Besides many others, the use of stannic silicate, zirconium phosphoantimonate, zinc ferrocyanide, stannic sulfosalicylate, binder free Zirconium (IV) antimonate and hydrous antimony (V) oxide layers have also been reported.

(e) Mixed Sorbents

Mixed layers (impregnated and non-impregnated) have been used by several workers for achieving enhanced resolution of components. Mixed layers are usually of medium activity as compared to the separated phases. The addition of kieselguhr in silica generally reduces the activity of silica, resulting in a new sorbent layer with altered activity that is capable of providing peculiar separations, not possible on separated phases. The binary layers that have been used include silica gel-microcrystalline cellulose (MCC) containing NH_4NO_3, silica gel G-MCC, silica gel-inorganic ion-exchange gels or Zr (IV) antimonate, MCC-modified silica gel H, silica gel - alumina or anitmonic acid and kieselguhr-cellulose.

(f) Miscellaneous Sorbents

The layer materials that are less familiar or introduced recently in TLC have been put under this category. These materials include silufol; silufor UV 254; silufol with a layer of silica gel; soil; soil-flyash mixture; soil treated with neutral, alkaline and saline solutions; polychrom A [porous copolymer of mixed 1,4 - and 1,5 - di-(methacryloyloxymethyl) naphthalene and styrene]; diatomite; chitin; chitosan and their derivatives as well as chitin modified with metal ions; carbamide-formaldehyde; kieselguhr and kaolin; polyamide; porous glass sheet; immobilized diazo-18-crown-6 and its N, O, S-containing analogs on silica support.

Mobile Phase *(Solvent System)*

With a particular sorbent layer, the separation possibility of a complex mixture is greatly improved by the proper selection of mobile phase. The mixture of organic solvents containing some aqueous acid, base or a buffer are, in general, well suited for the separation of ionic species whereas anhydrous organic solvents and water containing mobile phases are more useful for separating nonionic species. The following mobile phases have been used as developers :

(a) ***Inorganic Solvents :*** Solutions of mineral acids, bases, salts and mixtures of acids, bases and/or their salts.

(b) ***Organic Solvents :*** Acids, bases, hydrocarbons, alcohols, amines, ketones, aldehydes, esters, phosphates and their mixtures in different proportions.

(c) ***Mixed Aqueous - Organic Solvents :*** Above mentioned organic solvents mixed with water, mineral acids, inorganic bases or dimethylsulphoxide and buffered salt solutions.

(d) ***Complexing Solvents :*** Solutions of surfactants (SDS, CTAB, Triton x-100) and EDTA in various concentrations are used.

TLC with mobile phases of lower volatility gives better reproducibility compared to volatile mobile phases which have the advantage of quick evaporation from the sorbent layer after development.

1.9 VISUALIZATION

For visualization of separated zones on TLC plate physical, chemical or biological detection methods are commonly used. The physical detection methods are based on substance-specific properties and the most commonly employed methods of this group include the absorption or emission of electromagnetic radiation, autoradiography and X-ray fluorescence

microanalyses, etc. The chemical methods of detection involves the spraying of detection reagents capable of forming coloured compounds with the separated species on the chromatoplate or exposing the plate to vapours. Alternatively, the reagent can also be taken in the mobile phase or in the adsorbent. In some cases, the detection is completed by inspecting the TLC plate, after spraying with a suitable detection reagent, under UV light or by exposing the plates to ammonia vapours. Bioautographic analysis, reprint methods and enzymatic tests can also be applied for detection purposes. Immunostaining and flame ionization detection methods have been reported in recent past.

1.10 QUALITATIVE ANALYSIS

(i) Identification

In TLC the identification of separated compounds is primarily based on their mobility in a suitable solvent which is described by the R_F value of each compound, where

$$R_F = \frac{\text{distance of spot migration from the origin}}{\text{distance of solvent front from origin}}$$

The factors which influence the magnitude of R_F are: nature of sorbent, layer thickness, room temperature, sample volume, relative humidity and mode of development technique. Another term, R_M, which is the logarithmic function of the R_F value (i.e. $R_M = \log 1/R_F - 1$) is more useful as it bears a linear relationship to some TLC parameters or structural element of the analyte. However, in case of continuous and multiple development, where the solvent front is not measured, the term R_x $\left(R_X = \frac{\text{distance travelled by solute}}{\text{distance travelled by standard}}\right)$ is used.

If the retention data (R_F , R_M or R_X values) of the compound to be identified are identical with those of the reference substance in three

different solvent systems but on the same stationary phase or with the same solvent but on three different types of stationary phases, the two compounds can be regarded as identical with a good probability. However, for correct identification the chromatographic retention data are not enough and at least one spectroscopic method is necessary to make a valid statement.

(ii) Separation

When two or more analytes have differential migration with the same chromatographic system, they are mixed thoroughly, the mixture is spotted on the TLC plate and chromatographed. The separated components of mixture are detected and their R_F values are recorded. some of the basic requirements for a good separation are (a) each spot should be compact (R_L - $R_T \leq 0.3$), (b) the difference in R_F values of two adjacent spots should be atleast 0.1, (c) no complexation should occur between/among separable species and (d) chromatography of individuals and the mixture should be performed under identical experimental conditions.

1.11 QUANTITATIVE ANALYSIS

Methods for the quantitative evaluation of thin-layer chromatograms may be divided into two main categories : (i) quantitation after elution from the layer and (ii) *in-situ* quantitation on the layer. In the first, quantitation is performed after scraping off the separated analyte zone, collection of the sorbent and recovery of the substance by elution from the sorbent. Thereafter, the eluates are analyzed by applying any current method of microanalysis, such as electroanalytical, GC, spectrophotometry, titrimetry etc. In the second, solutes are assayed directly on the layer with the help of visual, manual or instrumental measurement methods. *In-situ* densitometry, a preferred technique for quantitative TLC involves the measurement of visible or ultraviolet absorbance, fluorescence or fluorescence quenching directly on the layer. The mea-

surements are made either by transmission through the plates, by reflection from the plate, or by reflection and transmission simultaneously, using either single beam, double-beam or single-beam-dual wavelength operation of scanning instruments. Modern optical densitometric scanners are linked to computer and are capable for automated peak location, multiple wavelength scanning and spectral comparison of fractions in several operating modes (reflectance, absorption, transmission, fluorescence etc.).

The careful combination of TLC with other analytical techniques has proved more useful for the analysis of complex samples. Spectrophotometry, HPLC, ICP, AES, voltammetery in conjunction with TLC are the most commonly used techniques. However, infra-red and thermal analytical techniques in combination with TLC have also been used.

For semiquantitative analysis, visual comparison and spot size measurement methods are used. A definite volume of sample is chromatographed alongside standards containing of analyte. After detection, the amount of analyte in the sample is estimated by visual comparison of the size and intensity of the sample zone with the standards. This method works well if the applied amounts of sample are kept close to the detection limit and the sample is accurately bracketed with standards. The shape and size of the spot produced on chromatograms are significantly influenced by the amount of analyte.

1.12 LITERATURE

Table 1.2 and 1.3 presents the work done in the field of TLC of inorganic and organic pollutants during 1991-1997.

Table 1.2 : Summary of Work Done on Inorganic TLC During 1991-97

Substance separated	Stationary phase	Mobile phase	Remarks	Ref.
Forty-nine inorganic ions	S_{14}	M_2	Qualitative separation	26
Inorganic ions	S_{15}	M_3	Selective separation of Re(VII) from many inorganic ions	27
Zr, Hf	S_1	M_4	Complete separation of Zr from mixtures containing Zr:Hf ratios ranging from 20:1 to 1:40	28
Several metal ions	S_2 , S_{16}	M_5	Separation of metal ions with different valency states	29
Fe, Ni, Zn, Cu, Pb, Mn	S_3	M_6	Separated metal ions were determined by atomic absorption spectroscopy	30
Forty-nine inorganic ions	S_{14}	M_7	Qualitative TLC	31
Ce^{2+}, Ce^{4+}, Nd, Eu, Gd, Tb, Yb, Y, Ti, V, Zr, Th	S_{17}	M_8	The R_F values of the lanthanide ions increase with increasing concentration of citric acid in the mobile phase	32

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Alkali Metals	S_{18}	M_9	Qualitative separations	33
Rare earth elements	S_{19}	M_{10}	Qualitative separations	34
Cu, Co, Cd, Hg, Ni, Ag	S_9 , S_{10}	M_{11}	Qualitative separations and determination of chromatographic parameters as a function of the concentrations of MeOH, NH_3, AcOH and inorganic salts in the mobile phase	35
Ni, Cu, Zn, Pd, Cd, Cr,Fe,Ru, Rh, La, Au, Tl, Zr, Pt, Nb, Ta, Mn, Ag, Hg, Co, Mo, W.	S_3 , S_{20}	M_{12}	Run 11cm; correlation between R_F values on impregnated layers developed with DMSO-THF (1+10) and the atomic numbers of the metal ions.	36
Transition Metal ions	S_9 , S_{10}	M_{13}	Qualitative TLC	37
Twenty-one inorganic cations	S_2	M_{14}	Separation and identification of cations on cellulose layers using six detection reagents	38

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
IO_3^-, IO_4^-, BrO_3^-, I^-, MoO_4^{2-}, $Fe(CN)_6^{4-}$	S_1	M_{15}	Effect of heavy metals on the chromatographic separation of periodate from iodate, bromate, iodide, molybdate and ferrocyanide	39
Eighteen anions	S_6 , S_{21}	M_{16}	Investigations of the effect of transition metals on the separations Cl^-–Br^-–I^- and NO_2^-–NO_3^-.	40
Seventeen anions	S_{22}	M_1	Qualitative separations	41
I^-, Br^-, NO_2^-, IO_3^-, BrO_3^-, NO_3^-, VO_3^-, MnO_4^{2-}, SCN^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, WO_4^{2-}, MoO_4^{2-}, Oxalate, PO_4^{3-}, $Fe(CN)_6^{3-}$	S_{23}	M_{17}	Microgram detection and separation of anions	42
Fe, Cu, Mn,	S_2	M_{18}	Qualitative separations	43
Pb, Cd, Zn	S_{24}	–	Application of TLC-square-wave anodic stripping voltametry for the determination of heavy metals.	44

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Mn, Co, Ni, Cu, Zn, Fe, Cr, Ti, V,	S_{13}	M_{19}	Reversed-phase TLC for qualitative identification of 3d metal ions.	45
Eleven metal ions	S_{25}	–	Retention behaviour of metal ions from aqueous solutions at pH 1-7 on impregnated silica layers	46
Metal ions	S_{27}	M_{20}	Qualitative separations	47
Mg, Al, Ca, V, Cu, Zn, Ge, Y, Zr, Mo, Ag, Cd, In, La, Ce, Eu, Tb, Tl, Pb, Bi	S_{28}	M_{21}	Detection limits and R_F values of fluorescent cations separated on porous glass sheet	48
Forty-nine inorganic ions	S_{29}	M_{22}	Separation of Sc(III), rare-earths(III), Y(III), Th(IV) and V(VI) from other ions	49
Fe, Co, Zn, Cd, Cu, Ni	S_{26}	–	Application to the analysis of alloys and natural water samples	50
Cd	S_{30}	M_{15}	Study of the influence of soil properties and constituents on the mobility of cadmium by soil TLC	51

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Rare elements	S_{12}	M_{23}	Preconcentration of rare-earths by circular TLC for subsequent ICP-AES determination in geological samples.	52
Toxic metal ions	S_1 , S_8 , S_{31}	M_{24}	Normal-phase, reversed-phase and chelation TLC of metal ions. Quantitative separation of Pb from binary mixtures and synthetic alloys.	53
Twenty-six transition and alkali metal ions	S_2	M_{26}	Qualitative separations	54
Heavy metals	S_{36}	–	Quantitative separation of Fe(III), Cu(II) and Pb(II) from other metals	55
Some Anions	–	–	Use of acid phosphates for detection and determination of certain anions	56
Some anions	S_3 , S_6 , S_4 , S_{21}	M_{15}	Qualitative separation; effect of $CaCl_2$, $MgCl_2$ and $NaHCO_3$ on the separation of anions; identification of NO_2^- in artificial sea water	57

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Cl^-, Br^-, I^-, ClO_3^-, ClO_4^-, $H_2PO_4^-$, NO_2^-, NO_3^-, SCN^-, SO_4^{2-}	S_{37}	M_{30}	Separation of inorganic anions as DMA (diantipyril methane) complexes and salts of protonated DMA using radial or ascending technique; determination of anion content by planimetry	58
Forty-nine inorganic ions	S_{32}	M_{22}	R_F value increase with increasing acid or sulfate concentration in the mobile phase	59
3d Series transition metal ions	S_{33}	M_{25}	Examination of the effect of the concentration of H_2MEHP and HNO_3 on R_F values	60
Uranium	S_{34}	M_{27}	Ascending technique; selective separation of uranium from synthetic mixture of several metal ions	61
Cations with some anions	S_{11}	M_{28}	Qualitative separations of cations and anions	62
Inorganic ions	S_{35}	M_{29}	Separation of polyvalent ions and rare-earths which tend to form anionic sulfate complexes	63

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Inorganic metal ions	S_{38}	M_{31}	Study on migration behaviour of metal ions under the influence pH of mobile phase and the concentration of impregnants.	64
Copper	S_3	M_{32}	Layer thikckness 0.25 mm, plate activation at 110°C, extraction of Cu from biological tissue by dry oxidation and ashing and chromatography on silica.	65
Hg, Cu, Cd	S_7	M_{33}	Temperature 25°C, UV spectroscopic determination of metal ions after elution with H_2O	66
Au, Ru, Rh, Pd, Os, Pt	S_1	M_{34}	Resolution (Rs) value of each pair of ions is 1.0 except that of Ru(III) and Pd(II), limit of detection is 4.0 μg	67
Inorganic ions	S_1	M_{35}	Relationship between volumetric % concentraiton (Cp) of IBMK/FA and the R_F values of ions is investigated	68

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Inorganic ions	S_4	M_{38}	Reactions of inorganic ions with organic reagents are studied on thin layers	69
Rore earths	S_{40}	M_{36}	R_F value of each metal decreased with increaseing pKa value of amine used for pretreatment	70
Actinides	S_{41}	–	Actinides are separated on the basis of different sorption behaviour in their ter-and penta-valancy states	71
Th, Fe, Al, Bi, UO_2, Cd, Hg, Ni, Co, Cu, Pb, Ag, Tl	S_{42}	M_{37}	Ascending technique, run 10 cm, layer thickness 0.25mm, limits of detection falls in the range of 0.22-3.4 μg	72
Cd, Zn, Cu, Pb	S_1	M_{38}	Ascending technique; run 10 cm; quantitative of Cu(II) by AAS after separation from other metal ions	73
Transition metal ions	S_{43}	M_{39}	Separation of eight component mixture and quantitative estimation by AAS	74

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
I^-, IO_3^-, IO_4^-, Br^-, BrO_3^-, NO_2^-, SCN^-, CrO_4^{2-}, PO_4^{3-}, MnO_4^-, WO_4^{2-}	S_{44}	M_{40}	Ascending technique, semiquantitation of I^-, Br^- and NO_2^- by spot area measurement	75
I^-, IO_3^-, IO_4^-, Br^-, BrO_3^-, NO_2^-, MnO_4^-, CrO_4^{2-}	S_1 , S_4 , S_5 , S_{45}	M_{41}	Ascending technique, run 10cm; semiquantitation of IO_4^- by peak height measurement	76
Thirty cations	S_{46}	M_{42}	Development time 19min; separation of Pt from 27 other cations	77
Cd, Cu, Pb	–	–	Detection limits for Cd and Pb is 1 and 4μg respectively	78
Heavy metal	–	–	Separation and identification of metals in human bones, placenta, milk and air by adsorption and IE-TLC	79
Ni, Co, Cu	–	–	Determination in rock samples by TLC/ photodensitometry; relative error ranging from 2 to 38%	80

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Co, Fe, Cu	S_{47}	M_{43}	TLC of metal ions on silica gel impregnated with chondroitin sulfate coated plates using plasma polymerization technique for coating the layer material	81
Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sn, Ta, Ti, V, Y, Zr.	S_{48}	–	ICP-AES determination of Zr in Zr-U alloys after separation by TLC	82
Metal cations	–	–	Determinaiton of Fe in process media by employing 8-hydroxyquinoline as complexing agent; Lumogallion was used in Al detection	83
Nine anions and eleven cations	S_{49}	M_{44}	TLC separation and colourimetric determination of SCN^- in water and wastewater	84

LIST OF STATIONARY PHASES

S_1 – Silica gel

S_2 – Cellulose

S_3 – Silica gel G

S_4 – Cellulose microcrystalline

S_5 – Alumina G

S_6 – Alumina

S_7 – Silica gel 60

S_8 – Silica gel loaded with various concentrations of TBA

S_9 – Chitin

S_{10} – Chitosan

S_{11} – Slilica gel impregnated with different concentrations of mono-2-ethylhexyl acid phosphate (H_2MEHP)

S_{12} – Fixion 50X8

S_{13} – Silical gel coated with high molecular weight amines (Primine JM-T, Amberlite LA-1, Alumina 36, Aliquat 336)

S_{14} – p-Aminobenzyl cellulose

S_{15} – Diethyl-(2-hydroxypropyl) aminoethyl QE-cellulose (strong basic anion exhanger)

S_{16} – Synthesized carbamide-formaldehyde polymer (aminoplast)

S_{17} – Silica gel coated with different concentrations of Primine JM-T

S_{18} – Zinc ferrocyanide

S_{19} – Diatomite

S_{20} – Silica gel impregnated with DMSO

S_{21} – Alumina - silica gel G (1:1, 1:2, 2:1)

S_{22} – Anhydrous antimony (V) oxide

S_{23} – Silica gel impreganted with 0.1% aq. solution of copper sulfate, zinc sulfate, nickel chloride, cobalt chloride, $Co(NH_3)_6Cl$

S_{24} – CM cellulose

S_{25} – Silica gel impregnated with a mixture of alizarin red S and aliquat 336

S_{26} – Silica gel modified with analog of dibenzo-18-crown-6

S_{27} – Mixtures of silica and inorganic ion-exchange gels

S_{28} – Porous glass sheets

S_{29} – Diethyl-(2-hydroxypropyl) aminoethyl cellulose

S_{30} – Soils with different characteristics

S_{31} – Silica gel impregnated with TBP

S_{32} – Arsenosilicates of Sn(IV), Cr(III) and Sb(V)

S_{33} – Silufol

S_{34} – Silica gel impregnated with high molecular weight amines

S_{35} – Silica gel impregnated with mono-2-ethylhexyl acid phosphate

S_{36} – Stannic sulfosalicylate

S_{37} – Trimethyl hydroxy propylamine cellulose (QA)

S_{38} – Surface-modified sorbent layers

S_{39} – Silica gel GF_{245}

S_{40} – Silica gel pretreated with amines {iminoie-2-ethanol; tris (hydroxymethyl) aminomethane; nitrilotri-2-ethanol and 1,3-diazole}

S_{41} – Silica gel impregnated with polyethylene glycol

S_{42} – Silica gel and alumina impregnated with 0.1-1.07 LiCl

S_{43} – Silica gel, plain and impregnated with EDTA (2%), dimethyl glyoxine (1%) or 1,10-phenanthroline (1%)

S_{44} – Silica gel, plain and impregnated with 1% aq. $CuSO_4$, alumina, kieselguhr, kaolin, alumina+celulose (2:1), kieselguhr + cellulose (1:2, 2:1)

S_{45} – Kieselguhr and kieselguhr + cellulose (4:1, 3:2)

S_{46} – Ce(III) silicate

S_{47} – Silica gel impregnated with sodium salt of condroitin sulfate

S_{48} – TBP coated polymeric supports

S_{49} – Cellulose microcrystalline, cellulose + kieselguhr (4:1, 3:2, 1:1); kieselguhr

LIST OF MOBILE PHASES

M_1 – Aq. organic acids

M_2 – H_2SO_4 (0.01-1.0M) and H_2SO_4 - ammonium sulfate (0.01 - 1.0M) systems

M_3 – Aq. HCl and HCl-ammonium chloride (0.01 - 1.0M) systems

M_4 – HNO_3 - HCl or H_2SO_4 containing different concentrations of hydrogen peroxide

M_5 – Eleven neutral and acidic solvent systems

M_6 – Aq. solutions of sodium thioglycolate (0.01 - 0.2M)

M_7 – Aq. HCl and aq. HCl - ammonium chloride mixtures

M_8 – 0.01 - 1.0 M citric acid

M_9 – Aq. ammonium nitrate

M_{10} – Solutions of acids, bases and salts

M_{11} – 1.0 M inorganic salt solutions in aq. methanol

M_{12} – DMSO - 1.0 M HNO_3 (1+1); DMSO-THF (1+10); n-butanol-acetone - HNO_3 (6+6+1); diisopropyl ether-DMSO (10+1) and DMSO-THF - diisopropylether systems

M_{13} – Several aq. mobile phases

M_{14} – Acetylacetone-acetone-conc. HCl (5+5+1)

M_{15} – Distilled water

M_{16} – Mixed acidic - organic solvent systems containing formic acid

M_{17} – Acetone - DMSO or formic acid, acetone - DMSO - formic acid and acetone-minreal acid mixtures

M_{18} – Ethanol-isobutanol-conc. HCl-water (12+6+1+1)

M_{19} – 0.001 - 0.1M aq. solutions of succinic acid

M_{20} – Sixteen different solvent systems

M_{21} – n-Butanol-benzene-1M HNO_3 - 1M HCl (75+69+4+2, v/v) or acetone - 3M HCl (99+1, v/v)

M_{22} – Aq. sulfuric acid and sulfuric acid - ammonium sulfate media

M_{23} – 0.1M $H_2C_2O_4$, 2M NH_4Cl, 5.0M HCl, 0.5M ammonium citrate

M_{24} – DMSO - HNO_3 and DMSO-HCl systems

M_{25} – HNO_3 at different concentrations

M_{26} – Four mobile phases

M_{27} – Mixtures of DMF and HNO_3 or HCl

M_{28} – Aq. MeOH containing tributylphosphate and formic acid

M_{29} – Sulfuric acid and organic solvents

M_{30} – Acetone - chloroform (3+1)

M_{31} – Formic acid and sodium formate

M_{32} – MeOH - AcOH (100 + 0.3, v/v).

M_{33} – Benzene - acetone - DMF (100:80:20)

M_{34} – HCl - acetylacetone mixtures

M_{35} – IBMK - formic acid

M_{36} – Aq. NH_4Cl solutions

M_{37} – Formic acid (1.0M), HCOONa (1.0M) and their mixture

M_{38} – HCOONa (1.0M) - KI (1.0M) in 1:9 ratio

M_{39} – Pyridine - benzene - HOAc - H_2O (6:5:8:4, 5:5:4:1); BuOH - benzene - formic acid (5:10:9)

M_{40} – Formic acid (1.0M); HCOONa (1.0M); double distilled water; HCl (1.0M) - acetone (1:9)

M_{41} – Water - in - oil microemulsion

M_{42} – 15 Solvent systems including NH_4OH (0.5M)

M_{43} – Aq. or organic solvents of different pH values

M_{44} – NH_4OH (1.0M) - acetone (1:9, 3:7:1:1, 7:3, 9:1)

Table 1.3 : Summary of Work Done on TLC of Aromatic Amines and Phenols During 1991-97

Substance separated	Stationary phase	Mobile phase	Remarks	Ref.
Indole	S_1	M_1	Indole has been successfully separated from carbazole and diphenylamine.	85
Substituted phenolic compounds	S_2	–	Good separation of substituted phenolic compounds.	86
Aliphatic and aromatic amines	S_3	M_2	An increase in the hydrophobic part of amines results in their increased retention on this sorbent	87
Aromatic amines	S_4	M_3	Effect of impregnant concentration, type of mobile phase and concentration of organic solvent in the mobile phase on the mobility of aromatic amines was studied	88
Indole and its derivatives	S_5	M_4	Separation and detection limits of indole derivatives examined	89

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Six aromatic amines	S_6	M_5	Method is highly reproducible and applied to the determination of amines in environmental sample	90
Phenolic Compounds	–	M_6	Determination of phenolic compounds in pharmaceuticals	91
Phenols and naphthols	S_7	–	Detection of phenols with seven organic chromogenic reagents	92
Phenols	S_8	M_8	Separation of phenols were achieved	93
Catecholamines	S_9	–	Determination of catecholamines in human urines.	94
Phenols and quinolines	S_6	M_{11}	Examination of retention patterns of phenols and quinolines	95
Ethylenediamine and its hydroxyethyl derivatives	S_6	M_7	Separation and determination of the test substances in air	96
Phenols	S_{10}	M_9	Separation and study of behaviour of phenols in normal and reversed-phase TLC	97

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Sixteen aromatic amines	S_{11}	M_{10}	The best separation was achieved with sodium dodecyl sulphate	98
Phenols	S_{10}	M_{12}	Examination of mobility of phenols by normal and reversed-phase TLC	99
Diphenylamine derivatives	–	–	Identification and isolation of diphenyl derivatives from smokless gunpowder.	100
Alkanolamines	S_{12}	M_{13}	Determination of capacity factors and and differentiation of alkanolamines	101
Aromatic amines	S_{13}	M_{14}	Identification and separation of aromatic amines	102
p-nitroanilines	S_{14}	M_{15}	TLC of p-nitroanilines and their analogs with cyclodextrins in the mobile phase.	103
Phenols	S_{15}	M_{16}	Qualitative separations	104
Aromatic amines	S_{16}	M_{17}	Qualitative separation of twenty-seven aromatic amines	105

Substance separated	Stationary phase	Mobile phase	Remarks	Reference
Biogenic amines	–	M_{18}	Detection and separation of 8 biogenic amines in fish sample by one-and two-dimensional TLC	106
Non phenolic primary and secondary amines	S_{17}	–	Detection of nonphenolic amines in in human urine samples	107
Phenolic compounds	S_{18}	M_{19}	Separation of different phenolic compounds from rapseed	108
Primary aromatic amines	S_{19}	–	Qualitative separations of 26 primary aromatic amines	109
Phenols	S_{20}	–	Separation and quantitative determination of pentachlorophenol in leather goods	110
Natural phenolic derivatives	S_6	M_{20}	Studies of chromatographic properties of phenolic derivatives	111

LIST OF STATIONARY PHASES

S_1 – Silica gel, alumina, cellulose and copper sulfate impregnated silica gel

S_2 – Silica gel containing $FeCl_3$ or $K_3Fe(CN)_6$

S_3 – Polyacrylonitrile

S_4 – Silica gel G impregnated with ammonium cerium (IV) nitrate

S_5 – 1% sodium CM-cellulose - silica gel G

S_6 – Silica gel

S_7 – Silica 60 + kieselguhr F_{254} , polyamide 11 F_{254}.

S_8 – Silica gel impregnated with $NaNO_2$

S_9 – NH_2 - modified silica gel

S_{10} – RP-8 and RP-18 silica gel

S_{11} – Silical gel G, silica gel G impregnated with 1% CTAB

S_{12} – Octadecyl silica

S_{13} – Silica gel, alumina, cellulose, cellulose-silica gel (4:1)

S_{14} – Silica gel and polyamide

S_{15} – Impregnated and non-impregnated silica gel

S_{16} – Silica gel G, silica gel G impregnated with aqueous solutions of various sodium salts

S_{17} – RP-18 HPTLC plates

S_{18} – Silica gel, cellulose, octadecyl silica

S_{19} – Fe(III) tungstophosphate

S_{20} – Aluminium sheets $RP18F_{254}$

LIST OF MOBILE PHASES

M_1 – Several aqueous and non-aqueous solvent system

M_2 – Seven aqueous solvent systems

M_3 – Organic solvents

M_4 – Petroleum ether-$CHCl_3$-Me_2CO (20:9:1); n-hexane-$CHCl_3$-Me_2CO (20:2:3); petroleum ether-Me_2CO (20:3.5); CCl_4-Me_2CO (20:2)

M_5 – 6-Amino-1-naphthol-3-sulfonic acid

M_6 – MeOH - Xylene (1:1)

M_7 – Ethanol-pyridine-25% ammonia mixture

M_8 – Aqueous and organic compounds in methanol or benzene

M_9 – Chloroform-isopropanol (49+1.5 v/v); benzne-methanol (8+1 v/v); benzene-isopropanol (50+4 v/v); methanol-water (2+1 v/v); methanol - 0.2 M NaOH (2+1 v/v)

M_{10} – Benzene - chloroform (40+60); 2% SDS; 3% Tween-20; 2% CTAB; chloroform-acetone-CCl_4

M_{11} – Dioxane or ethylacetate + heptane

M_{12} – Mixed organic and aqueous-organic solvents

M_{13} – Aqueous MeOH or MeCN

M_{14} – 0.1% Aqueous copper acetate

M_{15} – Aqueous mobile phases containing α–, β–, γ- and hydroxypropyl-β-cyclodextrin

M_{16} – Benzene-diethylamine (4:1 or 7:3)

M_{17} – Cyclohexane- benzene (1:4)

M_{18} – Benzene-triethylamine (5:1); benzene-triethylamine-acetone (10:2:1)

M_{19} – Benzene-methanol-acetic acid (45:8:4)

M_{20} – Mobile phases of different polarity.

1.13 CONCLUSION

From the above discussion it is clear that TLC/HPTLC has been a most dependable and useful analytical technique for the determination of inorganic and organic pollutants after their separation. From the literature presented in Tables 1.2 and 1.3, it is clear that very little work has been carried out on the chromatography of inorganic ions, phenols and amines using thin layers of inorganic ion-exchange materials. On the other hand, micellar-mediated mobile phase systems have almost been neglected in normal-phase or reversed-phase TLC.

The present work has three aims :

(i) To develop new layer materials by mixing inorganic ion exchanger gel with silica gel and to use these materials for important qualitative and quantitative separations of metal ions using both normal phase and reversed-phase TLC methods.

(ii) To search out novel mobile phases constituting microemulsion/ micellar system for achieving improved separations of organic and inorganic pollutants.

(iii) Quantitative estimation of cobalt and uranium after their separation from other metal ions.

Some interesting results achieved by the present studies are being presented in the following chapters.

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CHAPTER II

SEPARATION OF COEXISTING IRON, COBALT AND NICKEL IONS

2.1 INTRODUCTION

Mutual separation of iron, cobalt and nickel is of great importance for analytical, industrial, metallurgical and pharmaceutical applications. Though nickel is slightly poorer reductant but it forms many complexes similar to that of cobalt. Cobalt and Fe^{3+} together give a red brown precipitate with dimethylglyoxime (DMGO), the formation of which interferes in the detection of small amounts of nickel. The detection of Ni with DMGO is quite selective and very sensitive. The test fails, however, in ammoniacal or acetic acid solutions containing small amounts of nickel in the presence of cobalt because cobalt ions also react with DMGO to form soluble brown compounds of bi - and tervalent cobalt. DMGO is thus consumed by Co and not enough may be available to react with Ni, since the solubility of the reagent is quite limited. Furthermore, it is very difficult to visualize small amounts of the nickel precipitate in the cobalt.

Of the procedures used for the separation of inorganic ions, thin layer chromatography (TLC) is probably the most simple, lowest cost and highly effective separation technique. Several workers have used TLC, in the recent past for the separation of inorganics and organometallics (1,2). Solzic et al. (3) reported the systematic qualitative analysis of cations on the basis of R_F values, spot colours, spot shapes and the number of spots detected on microcrystalline cellulose layers with specific chromogenic reagents. Some studies have focused on the separation of inorganic ions on sorbent layers impregnated with liquid ion-exchanger by elution with HCl - ammonium thiocyanate (4,5), acidified LiCl and mineral acids (6-8). Hydrochloric acid - ammonium thiocyanate medium has been used by T. Shimizu et al. for the separation of numerous inorganic ions from multicomponent systems on thin layers of cellulose derivatives (9-11). An interesting study on the formation and chromatographic properties of thiocyanate complexes on alumina

layers developed with HCl-thiocyanate - $SnCl_2$ mixture has been reported (12). Thin layers of silica gel impregnated with ammonium thiocyanate have been used to study the chromotagraphic behaviour of inorganic pollutants in formic acid - sodium formate media (13). None of these studies refer to the separation of nickel from iron and cobalt or the separation of Fe^{2+} from Fe^{3+}.

The separations of Ni^{2+} from Co^{2+} and of Fe^{2+} from Fe^{3+} by TLC thus so far were not as good as desired. The separation distances, average ΔR_F values (difference in R_F values of Ni and Co) achieved by V.D. Canic et al. (14) on maize starch layer with butanol - pyridine - diethylaniline - 5N HCl; by Z. Solzic et al. (15) on a cellulose layer with acetone - conc. HCl - water (86:8:70); by U.A. Th.Brinkman et al. (6) with phenylpyrazole - HCl systems; and by A. Mohammad (16) on silica gel layer with formic acid containing solvent systems were 0.17, 0.24, 0.35 and 0.47 respectively, whereas the present method gives a ΔR_F value of 0.60 showing the formation of better resolved spots. In regards to Fe^{2+} - Fe^{3+} separation by TLC only two reports are available (17,18). It is therefore, worthwhile to develop new TLC methods for the separation of these metal ions from natural and synthetic water and waste water samples.

The present chapter is an attempt to develop a new TLC procedure for the separation of coexisting iron (II), iron (III), cobalt and nickel ions on TBP loaded ready made layers comprising mixture of silica gel and stannic arsenate gel using mixed inorganic solvent system containing hydrochloric acid, potassium thiocyanate and sodium chloride as developer. The detailed study of the various factors influencing the separation of iron - nickel - cobalt mixture is carried out. This work allows the application of reversed - phase TLC to the separation of nickel, cobalt and iron from acidic and ammoniacal solutions. The method can be extended to the identification and separation of these ions in rock, alloy, sea water and electroplating waste water samples.

2.2 EXPERIMENTAL

Apparatus : A TLC applicator (Toshniwal, India), glass plates (20×3cm), glass jars (24×6cm) and a digital pH meter CP901 were used.

Reagents : Stannic chloride pentahydrate, sodium arsenate, silica gel G, tri-n- butylphosphate (TBP), acetone, potassium thiocyanate, sodium chloride, hydrochloric acid, ammonium sulphide, potassium ferrocyanide, 1,10-phenanthroline (CDH, India); dimethlyglyoxime, acetic acid (Qualigens, India) were used. All other reagents were also of Analytical Reagent grade.

Metal Ions Studied : Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, VO^{2+}, UO_2^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Tl^{+}, Bi^{3+} and Hg^{2+}.

Test Solutions : Chromatography was performed on 1% standard solutions of the chloride, nitrate or sulphate salts of the above mentioned metal ions except Fe^{2+} for which 1% ferrous ammonium sulphate salt solution with 3 ml of H_2SO_4 and diluted to 1 litre was used.

Detection : Fe^{2+} was detected with 0.5% solution of 1, 10 - phenanthroline; Fe^{3+}, Cu^{2+}, VO^{2+}, UO_2^{2+} were detected with 1% potassium ferrocyanide; Ni^{2+} and Co^{2+} with 1% solution of alcoholic dimethylglyoxime; Zn^{2+} and Cd^{2+} with 0.5% dithizone in CCl_4 while Ag^{+}, Pb^{2+}, Tl^{+}, Bi^{3+} and Hg^{2+} were detected with 1% ammonium sulphide solution.

Solvent Systems : The following solvents (EDTA, acid and salt solutions were prepared in distilled water) were used as mobile phases:

M_1 = 1.0 M KSCN - 5.0 M HCl - 1.0 M NaCl (8:1:1) v/v
M_2 = 0.10, 0.50, 1.0 and 2.0 M KSCN
M_3 = 1, 3, 5, 7 and 10 M HCl
M_4 = 0.10, 0.50, 1.0 and 2.0 M NaCl
M_5 = 0.001, 0.01 and 0.1 M EDTA
M_6 = Acetone

M_7 = Isobutyl methyl ketone (IBMK)

M_8 = Ethyl methyl ketone (EMK)

M_9 = Methanol

M_{10} = Butanol

M_{11} = Isopropanol

M_{12} = 1.0 M NH_4SCN

M_{13} = 1.0 and 2.0 M Formic acid (FA)

M_{14} = DMSO - 1.0 M FA and DMSO - 2.0M FA
1:1, 1:3 and 3:1 ratio (v/v)

M_{15} = DMSO - acetone (1:1)

M_{16} = 1M NH_4Cl

M_{17} = 1 M LiCl

Stationary Phases : The stationary phases used for normal phase and reversed - phase TLC are given below :

S_1 = Silica gel G

S_2 = Dried stannic arsenate ion-exchanger

S_3 = Dried stannic arsenate ion-exchanger-silica gel G in 1:10, 10:1, 1:1 ratio (w/w)

S_4 = Stannic arsenate gel-silica gel G in 1:10, 1:5, 1:1 ratio (w/w)

S_5 = Stannic arsenate gel-silica gel G in 10:1 ratio (w/w)

S_6 = S_5 impregnated with 0.1, 0.5 1.0 and 2.0 M TBP in acetone

S_7 = S_5 impregnated with 0.2 M TBP in acetone

SYNTHESIS OF STANNIC ARSENATE ION-EXCHANGER

Stannic arsenate ion - exchanger was prepared as reported earlier (19) by mixing 0.1 M solutions of stannic chloride and sodium arsenate in a volume ratio of 3:2 and by digesting the resulting precipitate at room temperature for 24 hours. The gel obtained was washed several times with demineralized water. The gel is allowed to settle for some hours and excess water is then drained off. This ion - exchanger gel was used after mixing with the silica gel in a different weight ratio as

comprised the sorbent phase.

To obtain a dried stannic arsenate ion-exchanger, the ion-exchanger gel is dried at 80°C in an electrically controlled oven. The completely dried gel was washed with double distilled water which leads to cracking of the ion-exchanger in small granules of uniform size. The ion-exchanger is then kept in 1M HNO_3 overnight to convert it into H^+ form. After decantation, the ion-exchanger in the H^+ form was washed several times with water to make it free from acid and dried at 80°C.

PREPARATION OF THIN LAYER PLATES

(i) Plates of Stannic Arsenate Gel Mixed With Silica Gel

Stannic arsenate gel was mixed with silica gel G in 1:10, 1:5, 1:1 and 10:1 ratio (w/w) to make a homogeneous slurry in a mortar. This slurry was then spread over a clean glass plate (20×3 cm) by means of a TLC applicator (Toshniwal, India) to produce a 0.25 mm layer. The plates were air dried at room temperature and activated by heating at 100±2°C for 1 h in an electrically controlled oven. After activation, the plates were cooled to room temperature and stored in a closed chamber until used.

(ii) Plates of Pure Dried Stannic Arsenate Ion-exchanger and it's Mixture With Silica Gel G

TLC plates of pure dried stannic arsenate ion-exchanger and their mixture with silica gel G in 1:10, 10:1 and 1:1 ratio by weight were similarly prepared. For the preparation of TLC plates of pure stannic arsenate approximately 50 g of dried stannnic arsenate granules were mixed with 100 ml distilled water and the slurry was made by grinding the mixture vigorously in a glass mortar for a longer time. This step proved to be very important for proper adhesion. The resultant slurry in the form of a fine uniform paste was spread over the glass plates by TLC applicator to give a layer

0.25 mm thick. The plates were dried at room temperature and used as prepared. A set of prepared plates was activated at 100°C for 1 h but since slight cracking of coated ion-exchange material was observed these plates were not found suitable for use.

To prepare TLC plates by coating dried stannic arsenate mixed with silica gel, silica gel G was mixed with stannic arsenate in different weight ratio and the mixture was triturated well in a mortar with requisite volume of double distilled water to make a slurry of proper consistency. The slurry obtained was coated on glass plates to get a layer 0.25 mm thick. The plates were air dried at room temperature and activated at 100±2°C for 1 h in an electrically controlled oven. The plates were kept in closed chambers until used.

*(iii) **Preparation of TBP Impregnated TLC Plates***

The TLC plates prepared by coating a mixture prepared from stannic arsenate gel and silica gel G were impregnated with various concentrations (0.1-2M) of TBP. The plates were impregnated by developing with TBP solution of a required concentration in acetone and dried at room temperature followed by activation at 100°C as in the above mentioned case. A set of TLC plates was air dried and used without activation. After development, the detected spots on air dried plates show almost the same mobility with slightly more diffused spots compared to the spots on activated plates. Therefore, for obtaining more compact spots of metal ions we used activated plates for further studies.

The TLC plates of plain silica gel were prepared using the method reported earlier (20).

SAMPLE PREPARATION

(a) ***Spiked Water :*** 10 ml of distilled or drinking water was spiked with 1% solution of 5 ml Fe^{3+}; 10 ml of Co^{2+} and 5 ml of Ni^{2+} (i.e. 1:2:1 ratio v/v). The pH of this solution was 1.82. To 10 ml of this solution we pass ammonia to obtain a precipitate of these metals. The precipitate was separated by centrifugation, washed several times with distilled water, dried and dissolved in minimum volume of conc. HCl. To another part (10ml) of the spiked water we add 5 ml of pure acetic acid.

(b) ***Spiked sea water and industrial waste water :*** 15 ml of sea water collected from Kovalam Beach, Kerala, India, was spiked with 9 ml of 1% $CoCl_2$ + 6 ml of 1% $NiCl_2$ + 3 ml of 1% $FeCl_3$ solutions. To 5 ml of this spiked sea water we add 3 ml of pure acetic acid while to another 5 ml of this sample we add ammonia. A precipitate of metal hydroxides so obtained was separated out by centrifugation, washed and dissolved in conc. HCl.

20 ml of industrial waste water (collected from electroplating unit) is spiked with 10 ml of 1% $FeCl_3$ and 20 ml of 1% $CoCl_2$ solutions. To 10 ml of this spiked sample we add 5 ml of pure acetic acid and to another 10 ml we add ammonia to obtain a precipitate which was dissolved in conc. HCl after separation from the bulk and properly washed with distilled water.

(c) ***Spiked high speed steel sample :*** A part of the high speed steel sample was dissolved in a mixture of conc. HCl and conc. HNO_3 (1:1 v/v). 10 ml of this solution was diluted to 20 ml with distilled water and spiked with 5 ml of 1% Ni^{2+} solution. To 5 ml of this spiked sample we add 3 ml of pure acetic acid while to another 5 ml of spiked sample we add ammonia. The precipitate of metal hydroxides was separated out, washed and dissolved in conc. HCl.

(d) ***Spiked geological samples :*** To 10 ml each of the geological

samples AgV_1 Basalt USGS (United States Geological Survey, U.S.) and GSP_1, were spiked with 2 ml of 1% $CoCl_2$ and 1 ml of 1% $NiCl_2$ solutions. To 5 ml of each spiked geological sample we add 3 ml of pure acetic acid while to another 5 ml we add ammonia. A precipitate of metal hydroxides is obtained which is separated out from the bulk, dissolved in conc. HCl, digested by heating and the residue was dissolved in 2-3 ml of distilled water for both the samples (AgV_1 and GSP_1).

CHROMATOGRAPHY

Thin layer chromatography was performed on TLC plates coated with unimpregnated and TBP impregnated sorbent layers in 24×6 cm glass jars. Approximately 10 µL of standard test solutions were spotted separately on the TLC plates at 2 cm from the lower edge of the plate with the help of a micropipette. The spots were allowed to dry and then the plates were developed in the desired solvent system by the ascending technique keeping the solvent ascent upto 10 cm from the point of application at room temperature.

After development the plates were air dried at room temperature and the position of metal ions on the plates was identified by detecting the spots (i) as self detected coloured spots of Co^{+2} and Fe^{3+} and (ii) by spraying the appropriate reagent for other metal ions. R_F values were determined for the metal ions from the values of R_L (R_F of the leading front) and R_T (R_F of trailing front). Normal phase TLC was performed on S_1-S_5 stationary phases with different solvent systems whereas reversed - phase TLC was carried out on layers of S_1, S_6 and S_7. The effect of the concentration of TBP (0.01 M - 2.0M) as an eluent and as an impregnant was studied on S_5 stationary phase. The mobility of Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+}, was investigated with varying concentrations of KSCN, HCl and NaCl as mobile phase in order to select the proper solvent system for the four component separation Ni^{2+}– Co^{2+}– Fe^{2+} –

Fe^{3+}. The limit of detection of Ni^{2+}, Co^{2+} and Fe^{3+}, were determined by spotting 0.01 ml of cation solution of different concentrations on the chromatoplates which were developed with 1M KSCN, and the spots were visualized using appropriate detection reagent. This procedure was repeated with successive reduction of the concentration of the cation solution until no detection of the spot was possible. The minimum amount of metal salt just detectable in the solution was taken as the detection limit.

To study the effect of the pH of the test samples on the mobility and separation of metal ions, the pH of the standard solutions of the metals used or their mixture was brought to the required pH value by the addition of few drops of either dilute sodium hydroxide solution or dilute hydrochloric acid. The fixed volumes of Ni^{2+}, Co^{2+} or Fe^{3+} solution or their mixture in 1:1:1 ratio was adjusted to different pH values and were applied on the TLC plates. The plates were developed with M_1 and the R_F values of the metal ions were calculated after detection.

For studying the effect of some anions, amines and phenols on the separation of Ni^{2+} from Co^{2+}, synthetic mixtures containing Ni^{2+}, Co^{2+} and anion, amine or phenol solution in 1:1:2 ratio were prepared. The synthetic mixture solution was spotted on the chromatoplates and the plates were developed with 1M KSCN. The R_F values of Ni^{2+} and Co^{2+}, were determined and compared with the standard R_F values obtained in the absence of additives.

To study the loading effect on the R_F values of Ni^{2+}, the fixed volumes of various standard solutions of the metal salts were spotted on the TLC plates with the aid of a micropipette. The plates were developed with M_1 and R_F values were calculated. To investigate the effect of mineral or carboxylic acids, 5.0 M HCl in M_1 was replaced by other mineral or carboxylic acid of the same strength and the sep-

aration of Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} was monitored on S_7. Similarly, to examine the separation possibility of Ni^{2+} - Co^{2+} - Fe^{2+} - Fe^{3+} separation in the presence of other salt solutions, 1.0 M NaCl in M_1 was substituted by 1.0 M solutions of NH_4Cl, $(NH_4)_2SO_4$, $NaNO_2$, $NaNO_3$ or LiCl. The four - component mixture was chromatographed on S_7 and the R_F values of separated metal ions were recorded. For the identification of Ni^{2+}, Co^{2+}, and Fe^{3+} 0.01 ml of spiked water samples (acidic and ammoniacal) of sea water, industrial waste water, geological sample and high speed steel sample solutions were spotted on TLC plates (S_7), developed with M_1, detected with appropriate reagent and the R_F values of separated metal ions were determined.

2.3 RESULTS AND DISCUSSION

The main features of this study are (a) the use of silica gel G mixed with stannic arsenate gel as layer material, for normal phase and reversed - phase TLC, (b) the application of TBP as impregnant as well as eluent , (c) the separation of coexisting nickel, cobalt and iron ions from acidic and ammoniacal solutions, (d) effect of pH of sample, loading amount of analyte, presence of amines, phenols and anions on the separation of Ni^{2+} from Co^{2+} and (e) the identification and separation of Co^{2+}, Ni^{2+} and Fe^{3+} from distilled water, sea water, industrial waste water, high speed steel sample and geological samples.

The normal phase TLC with thin layers of pure stannic arsenate has been used earlier to get some interesting analytical separations (21-23). However, in our case the dried stannic arsenate ion - exchanger was found unsuitable for reversed - phase TLC since the plate made of pure dried stannic arsenate get deformed on impregnation with TBP. Our efforts to utilize this dried ion - exchanger as coating material after mixing with silica gel G failed as the preparation of homogeneous slurry to obtain good quality plates was very difficult. Besides this, the use

of inorganic ion-exchange materials as thin layers suffers the following main drawbacks: (a) The preparation of dried ion-exchanger is a very slow and lengthy process; (b) the yield of ion - exchanger is low and a large quantity of ion exchange material is required to prepare the TLC plates; (c) the time required for the development of the plate with most solvent system is, generally, longer and (d) the inorganic ion-exchange materials are not well characterized.

Therefore, we used the ion-exchanger in its gel form but since plates cannot be prepared with gel alone we added a sufficient quantity of silica gel G to obtain good quality, uniform and stable plates. Thin layers prepared from a mixture of stannic arsenate gel and silica gel G in 10:1 ratio w/w, was found most suitable stationary phase (S_5) for TLC of cations and this phase was selected for further studies using both normal phase and reversed - phase techniques. Some useful TLC separations of inorganic ions on combined thin layers of stannic arsenate gel and silica gel using mixed organic (24) and buffer solutions (25) as mobile phases have been achieved by Hussain et al. However, their studies were of a preliminary nature and suffer from the following limitations : (a) Comparative study on metal ions separations with mixed layers by normal phase and reversed-phase TLC has not been examined; (b) Effect of anionic and organic impurities on metal ions separation has not been studied; (c) Separation of co-existing Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} ions could not be achieved; (d) The method was not applied to real/ synthetic environmental and geological samples.

The proposed method describes a systematic approach to over-come the above limitations, offering useful knowledge for planning separations and putting the mixed layers to much practical use. Parallel researches in these media would provide interesting information about the ionic species in solution.

Normal phase TLC was performed on S_5 with several solvent systems (M_1-M_{17}) and it was observed that with increase in length of carbon chain (C_1 - C_4) in alcohols, both development time and tailing of the spots of metal ions increases while in case of ketones, increase in carbon chain length yields more compact spots leading to the selective separation of Hg^{2+} in ethyl methyl ketone. In fact, several mobile phases were found suitable for normal phase TLC but M_1 - M_4 and M_{16} yielded good results for reversed - phase TLC. Though TBP as impregnant improves the separation efficiency of S_5 but it's use as eluent results in unsatisfactory separations needing longer development time alongwith the formation of elongated spots for most of metal ions. In view of these observations, S_5 impregnated with TBP was selected for the present study as stationary phase.

To optimize the impregnant concentration, S_5 was impregnated at different concentration levels (0.01, 0.10, 0.20, 0.50, 1.0 and 2.0M) of TBP in acetone and the R_F values of metal ions were determined after developing the plates with M_1. The R_F values of all metal ions except Ni^{2+}, Ag^+ and Pb^{2+} decrease with increasing concentration of impregnation (i.e. the extraction increases with concentration of TBP). Ni^{2+} moves with the solvent front giving R_F value of 0.95 at all degrees of impregnation. Conversely, Pb^{2+} remains at the point of application over the entire concentration range of TBP. Ag^+ shows maximum mobility at 0.1M impregnation (R_F = 0.75) followed by decreasing trend in R_F value with the increase in impregnant concentration. Metal ions generally yield tailed spots in the impregnant concentration range of 0.5 to 2.0 M. The development time also increases from 15 min. (impregnant concentration, 0.2 M) with the increase in impregnant concentration to 15 h (impregnant concentration 2.0 M). Hg^{2+} could not be detected at any level of impregnation. Thus, the optimum concentration of impregnant was found in the range of 0.1 M < TBP < 0.5 M yielding the best results

at 0.2 M impregnant concentration. Therefore, S_5 impregnated with 0.2 M TBP (S_7) was found most suitable for reversed - phase TLC.

Though Ni^{2+} - Co^{2+} separation could be achieved on S_7 with 1M NH_4SCN, however, the use of 1.0 M KSCN instead of 1.0 M NH_4SCN provides better separation in terms of spot resolution and compactness. The effect of anions ($Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, SCN^- , VO_3^{2-} , WO_4^{2-} , MnO_4^- , CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , $Mo_7O_{24}^{6-}$, Br^- , IO_3^- , IO_4^-); amines (p and m-nitroaniline, m-phenylenediamine, aniline, α-naphthylamine, p and m-chloroaniline, indole, carbazole and diphenylamine); and phenols (β-naphthol, m-nitrophenol, resorcinol, hydroquinone and 8-hydroxyquinoline); on the separation of Ni^{2+} from Co^{2+} on S_7 using 1.0 M KSCN was also examined. The presence of most of the anions did not show any effect on the separation and the R_F values of Ni^{2+} and Co^{2+} remained unchanged but in the presence of CrO_4^{2-}, $Cr_2O_7^{2-}$,MoO_4^{2-} , $Mo_7O_{24}^{6-}$, Br^-, IO_3^- and IO_4^-, the detection of Ni^{2+} could not be realized and thus the separation is hampered by their presence in the mixture of nickel and cobalt. The presence of $Cr_2O_7^{2-}$ led to the formation of diffused spot for Co^{2+}. Amines and phenols have no effect on the separation. Although 3-chloroaniline caused tailing in the Ni^{2+} spot, it's presence did not harm the separation.

The chromatographic behaviour of metal ions at different concentrations of HCl and KSCN using S_7 as stationary phase is depicted in Figures 2.1 and 2.2. The R_F values for most of the metal ions (Bi^{3+} , UO_2^{2+}, VO^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+} and Pb^{2+}) fluctuate in between 0.8 and 1.0 over the entire concentration range of aqueous HCl (1.0 - 7.0M) showing the poor extraction of anionic chloro complexes of the metals by TBP. Conversely, Fe^{3+}, remained near the point of application in the concentration range of 3.0 - 7.0 M of HCl indicating the strong extraction of chlorocomplex. However, at 1.0 M HCl, Fe^{3+} migrates with the solvent showing R_F value of 0.75. The curves of R_F versus moles

of HCl (Fig 2.1) pass through a minima either at 3.0 or 5.0 M of HCl. Interestingly, this was the concentration range where we found slightly more compact spots and we selected 5.0 M HCl for further study. Though, Fe^{2+}, can be separated from Fe^{3+} on S_7 using 3-7 M HCl as mobile phase but Ni^{2+} and Co^{2+}, remain inseparable.

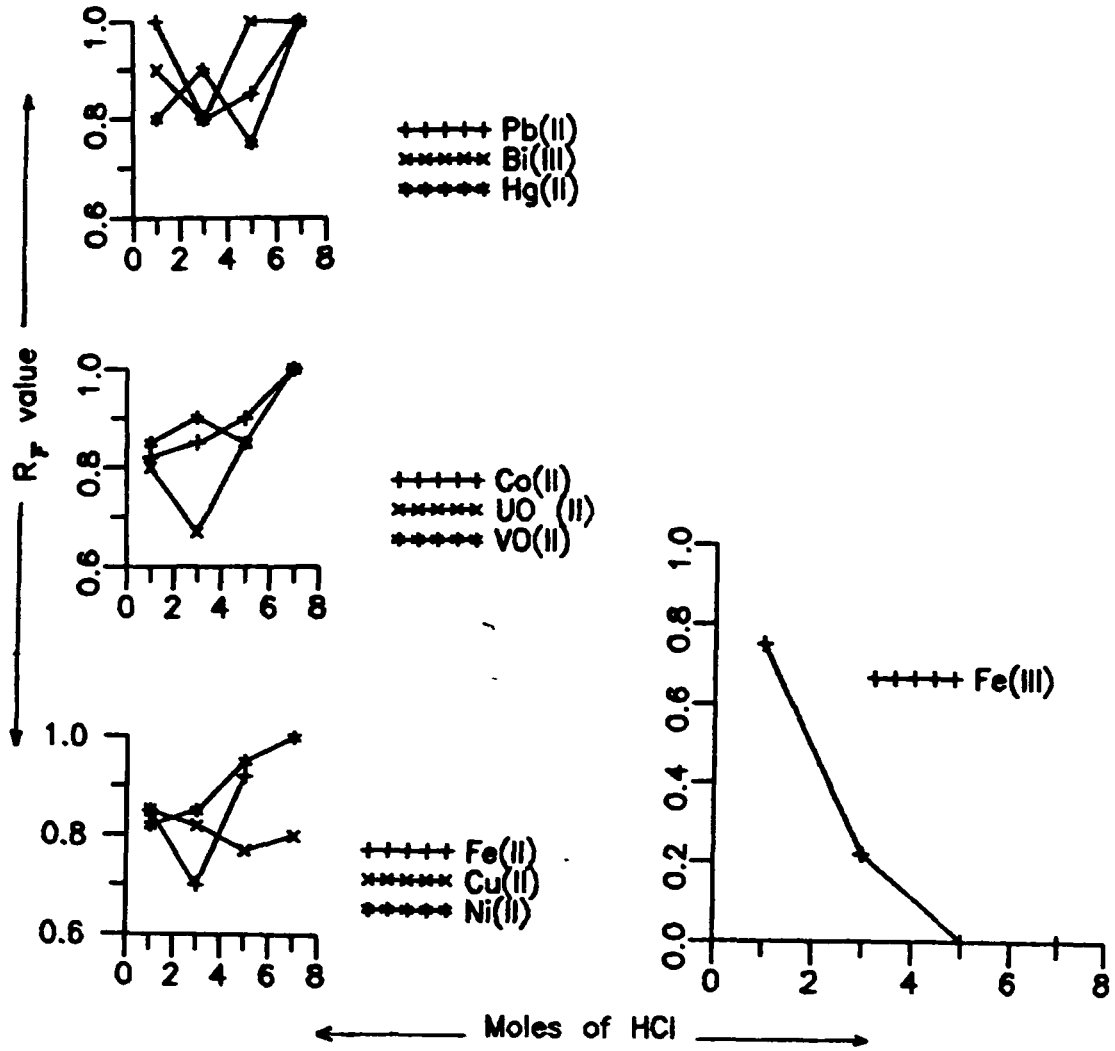

Fig. 2.1 The mobility of metal ions on S_7 developed with molar concentrations of HCl.

To understand the role of thiocyanate concentration on mobility, the metal ions were chromatographed on S_7 using aqueous developers containing varying molar concentrations of KSCN (0.10M - 2.0M). From the plot of R_F versus molar concentration of KSCN (Fig. 2.2), following trends are noticeable :

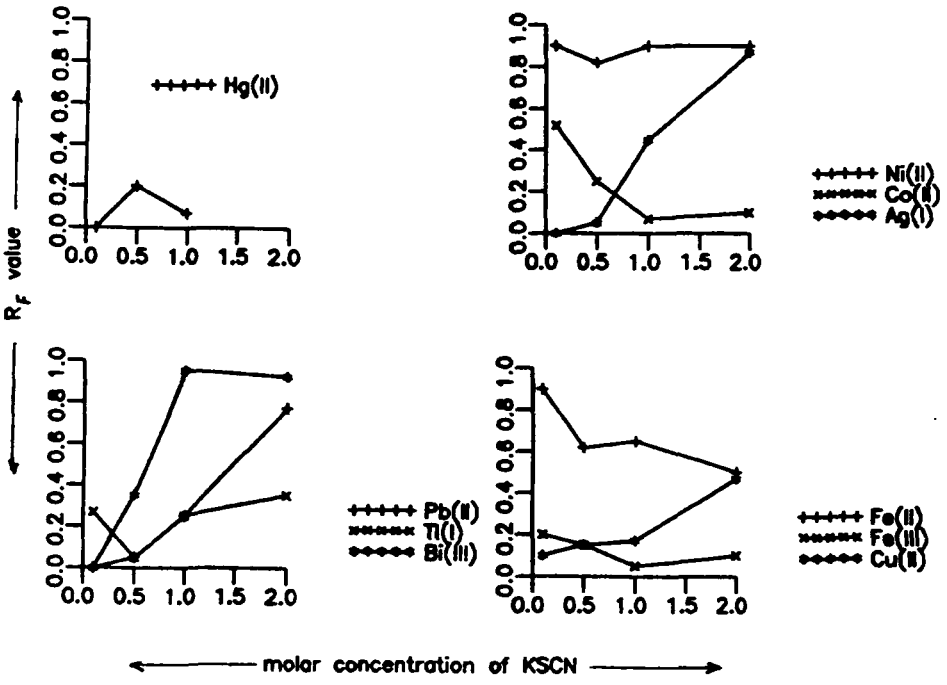

Fig. 2.2 The mobility of metal ions on S_7 developed with different molar concentrations of KSCN.

(a) Hg^{2+} and Tl^{+} remained near the point of application at all KSCN concentrations used. Conversely, Ni^{2+} moved with the solvent.

(b) The R_F of Pb^{2+}, Cu^{2+}, Ag^{+} and Bi^{3+} increased with the increase in KSCN concentration. These results are analogous with those obtained on paper impregnated with high molecular weight amines

using 0.5-7 M solutions of NH_4SCN as eluent (26). A reverse trend i.e. the decrease in R_F value with the increase in KSCN concentration was observed with Fe^{3+} , Co^{2+} and Fe^{2+} . This variation of R_F values with concentration of thiocyanate may be explained by a shift of the equilibrium of complex formation and the resulting shift in partition of the complex between two phases. These changes may also be effected by the addition of HCl to thiocyanate solution. As evident from Fig. 2.2., the separation of Ni^{2+} from Co^{2+} is possible with aqueous thiocyanate system but the separation of Fe^{2+} from Fe^{3+} is not good.

It is clear from the above discussion that while thiocyanate system is capable to separate Ni^{2+} from Co^{2+} , the HCl system is most suitable for the separation of Fe^{2+} from Fe^{3+} . Thus, the use of thiocyanate in combination with HCl furnished a novel solvent system for reversed - phase TLC of metal ions on TBP impregnated layers. As a result we achieved a very clear, reliable and reproducible separation of Ni^{2+} , Co^{2+} and Fe^{3+} from their mixtures. A mixture of 1.0 M KSCN and 5M HCl is capable to produce a very reliable three component separation of Ni^{2+}, Co^{2+} and Fe^{3+} . It is also possible to separate Fe^{2+} from Fe^{3+} with this solvent on S_7 layers. However, the addition of 1.0 M NaCl in this solvent system (5.0 M HCl + 1.0 M KSCN) further improves the separation of Ni^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} from their mixture. The results obtained after the variation of concentration of HCl (1-10 M) in a mixture of 1.0 M NaCl + 1.0 M KSCN and of KSCN (0.01 – 2.0M) in a mixture of 1.0M NaCl + 5.0 M HCl further confirms that a mixture consisting of 1.0 M NaCl, 1.0M KSCN and 5 M HCl in 1:8:1 ratio is the best solvent system for the separation of Ni^{2+} , Co^{2+} Fe^{2+} and Fe^{3+} (Figs. 2.3 and 2.4). The clarity of detection and compactness of spots increase with the increase in the concentration of KSCN in the mobile phase, yielding best results with 1.0 M KSCN - 5 M HCl - 1.0 M NaCl (8:1:1) as mobile

phase (M_1) and hence the chromatographic system, S_7 - M_1 was taken up as the best system for binary, ternary and quarternary separations of several metal ions including Ni^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} from their mixtures. At 2.0 M KSCN, Fe^{2+} produces double spots with R_F values of 0.5 and 1.0 (Fig 2.4) indicating the presence of two different species.

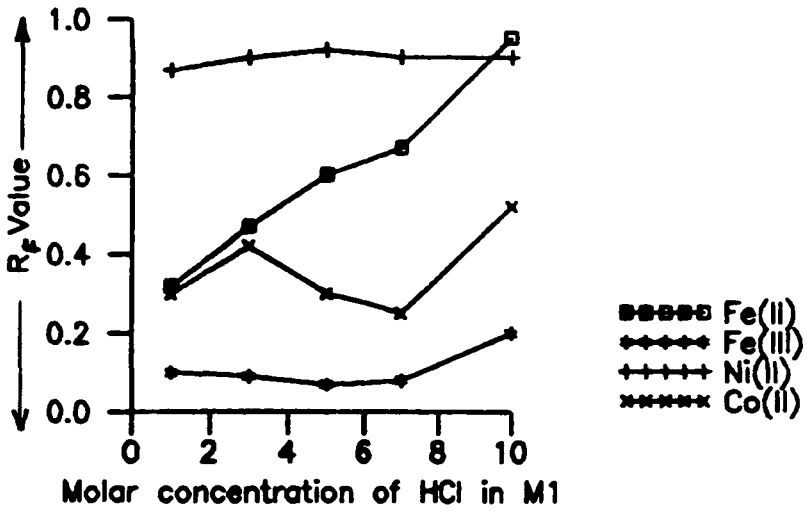

Fig. 2.3 Mobility of metal ions on S_7 developed with mixtures of 1.0 M KSCN and 1.0 M NaCl containing different molar concentrations of HCl.

These interesting separation possibilities arose from the following effects : (a) The presence of stannic arsenate in the silica gel to provide unique selectivity of the stationary phase, (b) potassium thiocyanate being an inorganic ligand is capable of forming thiocyanate complexes with several metals, (c) the presence of HCl may lead to the formation of chloro complexes and (d) the selective partitioning of metal complexes / metal ions into TBP.

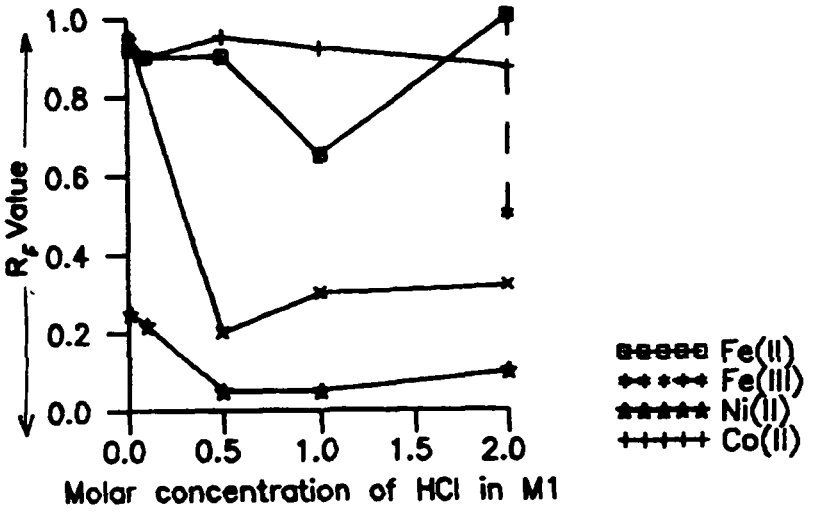

Fig. 2.4 Mobility of metal ions on S_7 developed with mixtures of 5.0 M HCl and 1.0 M NaCl containing different molar concentrations of KSCN.

In addition to the separations achieved experimentally (Table 2.1), the separation of Ni^{2+} from Co^{2+} is very important because both these ions have the same hydrated radii (3.0°A), almost similar electronegativity (Ni = 1.75, Co=1.70) (27) and non-spherical distribution of the d-electrons, i.e. Co(d^7) and Ni (d^8). Although the chromatoghraphic behaviour of metal ions can hardly be generally connected with their structural properties but it seems that the electronic configuration of 3d orbitals is reflected on the mobility of Co and Ni in the present case. Despite of the fact that Co and Ni have a non-spherical distribution of d-electrons, the R_F value of Ni (R_F = 0.98) is higher than that for Co (R_F = 0.30). This is because Ni has more d-electrons non-spherically distributed, i.e. 8 while Co has only 7, resulting in a greater shielding (causing higher mobility) in the case of Ni than in the case of Co.

TABLE 2.1: The Separations Experimentally Achieved With Different Mobile Phases on S_5 and S_7 Stationary Phases

Stationary phase	Mobile phase	Separation (R_F values)
S_5	M_5 (0.1M)	$Ag^+(0)$ - $Pb^{2+}(0.85)$, $Tl^+(0.15)$ - $Pb^{2+}(0.85)$, $Ag^+(0)$ - $Bi^{3+}(0.85)$, $Tl^+(0.15)$ - $Bi^{3+}(0.85)$
	M_8	$Hg^{2+}(0.90)$ - Fe^{3+}/ Cu^{2+}/ Co^{2+}/ Ni^{2+}/ UO_2^{2+}/ VO^{2+}/ Ag^+/ Pb^{2+}/ Tl^+/ $Bi^{3+}(0)$
	M_{12}	$VO^{2+}(0.98)$ - $Pb^{2+}(0)$, $VO^{2+}((0.98)$ - $Tl^+(0.10)$, $Zn^{2+}(0.90)$ - $Pb^{2+}(0)$, $Zn^{2+}((0.90)$ - $Tl^+(0.10)$, $Ag^+(0.95)$ - $Pb^{2+}(0)$, $Ag^+(0.95)$ - $Tl^+(0.10)$
	M_{15}	$Hg^{2+}(0.50)$ - Fe^{3+}/ Cu^{2+}/ Ni^{2+}/ UO_2^{2+}/ VO^{2+}/ Cd^{2+}/ Zn^{2+}/ Pb^{2+}/ $Tl^+(0)$
	M_{16}	$Co^{2+}(1.0)$ - $Pb^{2+}(0)$, $Co^{2+}(1.0)$ - $Ag^+(0)$, $Co^{2+}(1.0)$ - $Tl^+(0)$, $Bi^{3+}(0.85)$ - $Pb^{2+}(0)$, $Bi^{3+}(0.85)$ - $Ag^+(0)$, $Bi^{3+}(0.85)$ - $Tl^+(0)$
	M_{17}	$Ni^{2+}(1.0)$ - $Pb^{2+}(0)$, $Ni^{2+}(1.0)$ - $Ag^+(0)$, $Ni^{2+}(1.0)$ - $Tl^+(0)$, $Co^{2+}(1.0)$ - $Pb^{2+}(0)$, $Co^{2+}(1.0)$ - $Ag^+(0)$, $Co^{2+}(1.0)$ - $Tl^+(0)$
S_7	M_1*	$Ni^{2+}(0.90)$ - $Ag^+(0.55)$ - $Pb^{2+}(0.05)$, $Ni^{2+}(0.90)$ - $VO^{2+}(0.50)$ - $Pb^{2+}(0.01)$, Ni^{2+} (0.95) - $Bi^{3+}(0.60)$ - $Pb^{2+}(0.00)$, $Ni^{2+}(0.98)$ - $Ag^+(0.50)$ - $Fe^{3+}(0.15)$, $Ni^{2+}(0.90)$ - $VO^{2+}(0.52)$ - $Fe^{3+}(0.10)$, $Ni^{2+}(0.85)$ - $Bi^{3+}(0.60)$ - $Fe^{3+}(0.10)$, $Ni^{2+}(0.92)$ - $Co^{2+}(0.20)$ - $Pb^{2+}(0.00)$, $Ni^{2+}(0.95)$ - $Co^{2+}(0.30)$ - $Fe^{3+}(0.10)$
	M_2 (1.0M)	$Ni^{2+}(0.95)$ - $Co^{2+}(0.07)$, $Bi^{3+}(0.95)$ - $Hg^{2+}(0.07)$
	M_3 (5.0M)	$Fe^{3+}(0.10)$ - $Cu^{2+}(0.77)$, $Fe^{3+}(0.10)$ - $Fe^{2+}(0.85)$

* Development time ~ 24 min.

Further, the order of R_F values of Ni and Co is the same as the deviation (28) of their ionic radii (ΔR) from their theoretical value which is effected by the configuration of the ion. ΔR is zero where the electrons in the d-orbital are spherically distributed and the shielding is less. However, if the distribution of the d-electrons is non-spherical (i.e. shielding is more), there is more deviation from the theoretical values as in the case of Ni (ΔR = 0.7) and Co (ΔR = 0.5).

Another important aspect of the present study is the separation of Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} from their mixture. The order of R_F values and the separation sequence of these metal ions on S_7 with M_1 is as follows : Ni^{2+} (0.98) > Fe^{2+} (0.65) > Co^{2+}(0.30) > Fe^{3+} (0.1). The approximate R_F vlaues are given in parenthesis. The absence of sorption in the case of Ni^{2+} may be attributed to the lack of formation of anionic thiocyanate complex under the specified experimental conditions. In fact we could not realize the characteristic green Ni-thiocyanate complex on mixing of nickel solution with the mobile phase (M_1). In the case of Co^{2+}, a blue coloured tetrathiocyanato cobaltate (II) ion $[Co(SCN)_4]^{2-}$ is formed which showed maximum absorbance at λ_{max} 630 nm. This complex exhibits moderate extractibility into TBP giving R_F value of 0.30. The blue colour fades in the water but stabilized with thiocyanate solution. With Fe^{3+}, a cationic dark red complex, $Fe(SCN)^{2+}$ is formed as expected in acidic aqueous medium (29), which is strongly extracted by TBP and remains at the point of application (R_F = 0.10). Compared to Fe^{3+}, Fe^{2+} shows higher R_F (i.e. poor extraction) facilitating another important separation Fe^{3+} from Fe^{2+}. This behaviour may be explained on the basis of the relative stability of complexes of ions of different valency states. In the case of iron complexes with organic as well as inorganic anions, generally, the complex of Fe^{3+} has a higher stability constant (29). Thus, Fe^{3+} complex being more stable shows less mobility (i.e. low R_F) compared to less stable complex of Fe^{2+} which shows higher

R_F values (R_F = 0.65). The higher charge on Fe^{3+} also favours the smaller R_F for Fe^{3+} (30). A similar trend in R_F values for Fe^{3+} (R_F = 0.24) and Fe^{2+} (R_F= 0.45) was observed by Perisic Janjic et al. (31). An inverse correlation between percent extraction (%E) and hR_F values of metal ions has been reported by A. Jain et al. (32).

The substitution of HCl in solvent M_1 by mineral or carboxylic acids hampered the four - component separation of Ni^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} (Table 2.2). However, the tailing reducing nature of formic acid facilitates the formation of spots with increased compactness; and therefore, clearer detection and better binary separations of Ni^{2+} from Co^{2+} and of Fe^{2+} from Fe^{3+} . These separations could also be achieved with acetic acid instead of HCl or HCOOH. These acids can be put in the following preferred order if used as eluent in combination with KSCN and NaCl : HCl > HCOOH > CH_3COOH > H_2SO_4.

TABLE 2.2: Effect of Mineral or Carboxylic Acids on the Separation of Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} From Their Mixture on S_7

Mobile Phase : IM KSCN +5M Acid + 1M NaCl (8:1:1)

Metal Ions	hR_F values (R_F×100)			
	HCl	H_2SO_4	CH_3COOH	HCOOH
Fe^{2+}	60	82	55	60
Fe^{3+}	05	20T*	00	00
Ni^{2+}	90	90	80	90
Co^{2+}	30	60	05	00

* T = Tailed spot

Similarly, the four - component separation is harmed if NaCl in M_1 is replaced with LiCl, NH_4Cl, $(NH_4)_2SO_4$, $NaNO_2$ or $NaNO_3$ (Table 2.3). The preferred order of using these salt solutions in combination with HCl and KSCN is : NaCl > $NaNO_3$ > LiCl = $NaNO_2$ > NH_4Cl > $(NH_4)_2SO_4$. This particular observation is not in full agreement with Janjic et al. (33) who, on the basis of literature data about the performance of aqueous salt solutions as mobile phases in salting out TLC

concluded that, *"ammonium sulphate and to lesser extent sodium chloride, proved during the years to be better than other investigated salts"*. The use of $NaNO_2$ with M_1 is not useful as it furnishes the colour to the mobile phase and TLC plates are changed to yellow after development.

TABLE 2.3: Effect of Different Salts on the Separation of Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} From Their Mixture on S_7

Mobile Phase : IM KSCN +5M HCl + 1M Aq. salt (8:1:1)

Metal Ions	hR_F values ($R_F \times 100$)					
	NaCl	LiCl	NH_4Cl	$NaNO_2$	$NaNO_3$	$(NH_4)_2SO_4$
Fe^{2+}	60	00	35T*	00	60	80
Fe^{3+}	05	00	35T	00	07	25T
Ni^{2+}	90	90	90	9	92	87
Co^{2+}	30	30	17T	17T	25T	20T

* T = Tailed spot

It is evident from Fig. 2.5 that R_F values of the cations are less or more independent of the pH of sample of mixtures of Ni^{2+}+Co^{2+}+Fe^{3+} and Ni^{2+} + Co^{2+} between the pH limits of 1.0 to 4.2 and 1.0 to 6.0 respectively. Therefore, Ni^{2+} can be separated from Co^{2+} and Fe^{3+} without need for close control of pH of the sample. At pH 4.2 of sample mixture, Fe^{3+} is partially hydrolysed while Ni^{2+} and Co^{2+} remains in the form of ions. At pH 7.6, Fe^{3+} and Ni^{2+} get precipitated alongwith partial hydrolysis of Co^{2+} . At pH ≥10 all the three metals are completely converted into hydroxides. The precipitates obtained at pH 10.5 and 12.2 were dissolved in minimum amount of conc. HCl, diluted with water and subjected to TLC. All the three metal ions were clearly resolved on TLC plates in the identical separation sequence i.e. Ni^{2+} (R_F = 0.95), Co^{2+} (R_F = 0.3) and Fe^{3+} (R_F = 0.05). Thus, this method can be applied for the separation of Ni^{2+} , Co^{2+} and Fe^{3+} from acidic and alkaline sample solutions.

The effect of loading amount on the R_F values was studied and the lowest possible detectable amount of metal ions on the chromatoplates

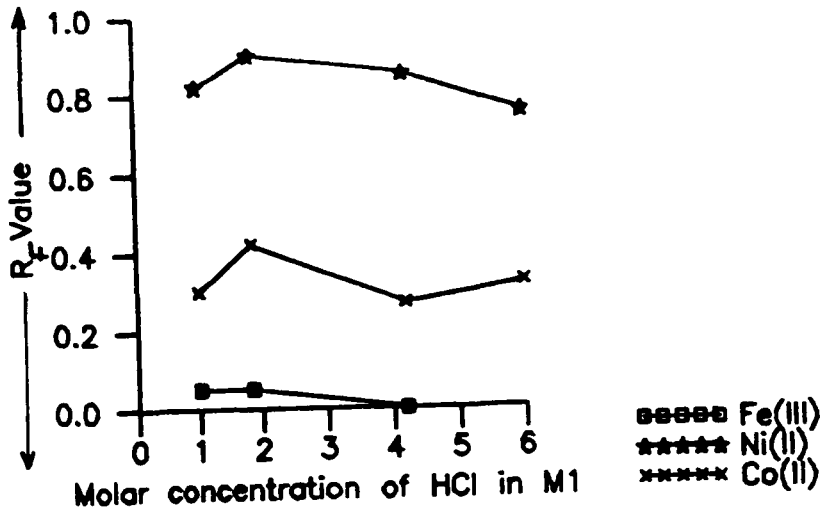

Fig. 2.5 Mobility of metal ions at different pH values of sample solutions.

was determined. As the amount of the metal ion loaded increases the length of the spot increases. It is always possible to separate a reasonable amount of Ni^{2+} from microrgram quantities of Fe^{3+} since 2.4 μg of Ni^{2+} gave R_F equal to 0.95, while it is 0.85 for 25.0 μg of Ni^{2+} . The proposed method is sensitive for the detection of Ni^{2+} (2.47 μg), Co^{2+} (2.02 μg) and Fe^{3+} (1.72 μg) as their chloride salts.

APPLICATION

The proposed method was applied to separate, detect and identify nickel, cobalt and iron (III) from various water samples. The detection of Ni^{2+} from electroplating waste water, Fe^{3+} from rock sample and Fe^{3+} and Co^{2+} from high speed steel sample was possible by directly spotting 0.01 ml of these samples on TLC plates. The TLC of spiked samples (acidic and ammoniacal) by the above method yielded clear detection, identification and separation of Ni^{2+}, Fe^{3+} and Co^{2+} on TLC plates.

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CHAPTER III

DETERMINATION OF COBALT WITH PRELIMINARY SEPARATION FROM NICKEL

3.1 INTRODUCTION

Separation of cobalt from nickel is important from analytical point of view as it forms many complexes similar to nickel. Nickel salts form a bright red insoluble inner complex with dimethylglyoxime (DMGO) and this colour reaction provides quite a selective method for sensitive detection of nickel. However, the presence of cobalt which forms brown compounds with DMGO interferes in the detection of nickel at microgram level. Since the solubility of the reagent is limited, enough DMGO may not be available to react with nickel in the presence of cobalt in solution. Thus, the separation of cobalt from nickel assumes significance in colourimetric analysis of a variety of samples containing nickel.

Amongst the methods available for the analysis of inorganic ions, thin layer chromatography (TLC) is the most useful technique due to (i) low cost, (ii) minimal sample clean up, (iii) wide choice of mobile phases, (iv) flexibility in sample detection, (v) high sample loading capacity and (vi) easy handling. Metal ions have been analyzed on silica gel layers impregnated with high molecular weight amines (1-10), organophosphorous compounds including TBP (11-13), dimethylsuphoxide (14), and a mixture of alizarin red S and aliquat 336 (15). Thin layers of unimpregnated stannic arsenate ion-exchanger (16-18) and mixture of silica gel and ion-exchange gels (19) have also been utilized for achieving new separations of metal ions. However, no work is reported on the use of TBP impregnated mixed layers prepared from mixture of silica gel and stannic arsenate gel. This study reports a suitable support for TBP which can be utilized in qualitative as well as quantitative analysis of inorganic ions.

3.2 EXPERIMENTAL

Apparatus : A TLC applicator (Toshniwal, India); [illegible] plates (20×3cm) glass jars (24×6cm), digital pH meter CP 901 and spectronic 20 spec-

trophotometer (Bausch and Lomb) were used.

Reagents : Stannic chloride pentahydrate, sodium arsenate, silica gel G, tri-n-butylphosphate (TBP), acetone, potassium thiocyanate were obtained from CDH, India and dimethylglyoxime was from Qualigens, India. All other chemicals used were also of analytical grade reagents.

Test Solutions : 1% standard solutions of nickel chloride and cobalt nitrate were used for all chromatographic and quantitative studies.

Detection Reagents : Both cobalt and nickel were detected on the plates by spraying with 1% alcoholic dimethylglyoxime.

Chromatographic System : The chromatographic system used comprises of 1M potassium thiocyanate (KSCN) as mobile phase and a mixture of stannic arsenate gel and silica gel G in the ratio 10:1 (w/w) impregnated with 0.2M TBP as stationary phase.

SYNTHESIS OF STANNIC ARSENATE ION - EXCHANGER GEL

Stannic arsenate ion-exchanger gel was prepared by mixing 0.1M solutions of stannic chloride and sodium arsenate in the volume ratio of 3:2 and digesting the resulting precipitate at room temperature for 24 hours. The gel so obtained was washed several times with demineralized water and allowed to settle for some hours. The excess water was drained off. The ion-exchanger gel was used after mixing with silica gel G in suitable weight ratio as mixed sorbent phase.

CHROMATOGRAPHY

Preparation of Thin Layer Plates

Stannic arsenate gel was mixed with silica gel G in 10:1 ratio (w/w) to make a homogeneous slurry in a mortar. The slurry so obtained was coated on a clean glass plate (20×3cm) by means of TLC applicator to produce layer of 0.25 mm thickness. The plate was air dried at room

temperature (30°C) and activated by heating at 100±5°C for 1 h in an electrically controlled oven followed by cooling at room temperature and stored in a closed chamber until used. The layers prepared from a mixture of silica gel and stannic arsenate containing silica gel exceeding 10% were of inferior quality. The coated plates were impregnated with 0.1 - 0.5 M TBP solution in acetone by developing the plates with TBP solution of required concentration. The impregnation with 0.2M TBP was found most suitable.

PROCEDURE

Thin layer chromatography was performed on TLC plates coated with TBP (0.2M in acetone) impregnated sorbent layers in 24×6cm glass jars. 10μL standard solutions of Ni and Co were loaded separately on the plates at a distance of 3cm above from the lower edge of the plate with the help of a micropipette. After drying the spots at room temperature, the plates were developed in the solvent system (1M KSCN) by keeping the solvent ascent as 10cm from the point of sample application. After development, the plates were dried and the position of nickel ion on the plates was identified by spraying TLC plate with alcoholic dimethylglyoxime (1%). The presence of cobalt ion on the plates was noticed visually as blue coloured spot. The well resolved and brightly coloured single spots of cobalt ($R_F \geq 0.10$) and nickel ($R_F \geq 0.96$) were stable enough on the layer for a long period at room temperature.

The following studies were carried out to identify optimum experimental conditions for realizing the best separation of cobalt from nickel.

(a) To study the effect of alkalinity and acidity of sample on the separation of cobalt from nickel, the pH of the standard solutions of the concerned metals or their mixture (1:1, v/v) was brought

in the basic or acidic range by adding required volumes of 1M ammonium hydroxide or 10% HCl. The resulting sample solution (10μL) was loaded on the TLC plates with a micropipette and the chromatography was performed as described above.

(b) To observe the effect of surfactants on the separation, sample solution was prepared by mixing standard solutions of cobalt and nickel with aqueous sodium dodecyl sulphate (SDS) or N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) in the volume ratio of 1:1:1. 10μL of this solution was loaded on the chromatoplates for chromatography.

(c) The possibility of preconcentration and microgram separation of cobalt from nickel (from water samples) were investigated as follows. 20mL distilled water was spiked with 100ppm of Ni and 50ppm of Co. The resulting solution was mixed with excess ammonium sulphide. Metal ions present in the solution are concentrated as black precipitate. The precipitate was collected after centrifugation and washed with distilled water, dried and dissolved in minimum volume of aqua regia. The solution was then evaporated to dryness and the precipitate so obtained was dissolved in about 1mL of dilute hydrochloric acid (10%). This solution (10μL) was subjected for chromatographic separation of cobalt from nickel.

Spectrophotometric Determination of Cobalt

Spectrophotometry of cobalt after TLC separation from nickel was carried out as follows. A sample of cobalt solution containing 49.4 to 345.8μg of cobalt was treated with 0.1 mL of 1M KSCN and the volume was made upto 25mL with dimethylformamide (DMF). After thorough mixing the solution was left for about 5 minutes for complete color development. The absorption spectra of this solution against reagent

blank over 360-700 nm gave a maximum absorbance peak at 630 nm (λmax.) The colour produced with cobalt was stable and proportional to the cobalt concentration. The recovery of cobalt after separation from nickel was determined as follows. Different volumes (7 samples) 0.02 - 0.14 mL of the sample solution containing 49.4 to 345 μg cobalt were mixed with ~25μg of nickel (in each sample) and loaded on to chromatoplates. The spots were dried at room temperature and developed in 1M KSCN system. After development, the plates were dried at room temperature and the area covering the spot of cobalt thiocyanate complex was scraped off from the plate into a clean beaker. This portion of adsorbent was washed several times with diethylether to remove tributyl phosphate followed by complete removal of ether by evaporation. The solute was then extracted from the sorbent into 10-15 mL DMF and the total volume was made upto 25mL by adding DMF. The absorbance of this solution was measured at 630 nm against reagent blank using 1cm cell. The measurement was repeated at different time intervals. The percentage recovery of cobalt after its separation from nickel was then determined from the recovery curve obtained by plotting absorbance against amount of cobalt. Percentage recovery was calculated using the following relationship.

$$\text{Percentage recovery} = 100 - K$$

$$\text{Relative error (K)} = \frac{X_i - X_t}{X_t} \times 100$$

Where X_i is the amount of cobalt obtained after extraction from adsorbent and X_t is the amount of cobalt loaded on the TLC plate.

3.3 RESULTS AND DISCUSSION

Stannic arsenate has been used in column chromatography (20) and normal planar chromatography for the analysis of metal ions (16-18). However, its use in reversed-phase TLC has not been examined yet. The papers reported on planar chromatography with stannic arsenate

layers did not mention the separation of Co^{++} from Ni^{++} because of their very similar chemical properties. In our case, Co^{++} (R_F = 0.05) could be very well separated from Ni^{++} (R_F = 0.96) only on TBP impregnated layers (i.e. reversed-phase TLC) whereas both the ions co-migrate on unimpregnated layers (i.e. normal TLC) when developed in aqueous potassium thiocyanates. Blue coloured Co-thiocyanate complex is strongly extracted in TBP and remained at the point of application whereas nickel is not extracted by TBP from aqueous solutions or from thiocyanate solution and migrates with the solvent front.

Results of the present study established a useful combination of TBP impregnated mixed sorbent layer i.e. stannic arsenate gel-silica gel G (10:1, w/w), with aqueous potassium thiocynate solution as mobile phase for the selective separation of nickel from cobalt. Ni^{++} moves with the solvent front giving $R_F \geq 0.96$ irrespective of the concentration of TBP used. Co^{++} remained almost at the point of application ($R_F \leq 0.10$). The optimum impregnant concentration was found in the range 0.1M - 0.5M with the best results at 0.2M. The system comprising of stannic arsenate gel-silica gel G (10:1, w/w) impregnated with 0.2M TBP as stationary phase and 1.0M KSCN as mobile phase is selected for detailed study.

The chromatographic behaviour of cobalt and nickel in the presence of different concentration levels of surfactants and effect of acidity and alkalinity of the sample are shown in Table 3.1. From this Table, it is clear that Co^{++} is well separated from Ni^{++} in the presence of HCl and NH_4OH i.e. in the acidic and basic pH range. However, the detection of nickel becomes trivial in the presence of HCl.

Table 3.1 : Effect of Acidity, Alkalinity and Presence of Surfactants in the Sample on the Chromatographic Behaviour of Co^{++} and Ni^{++}

	Sample used	Separation (R_L - R_T values)	Remarks
(a)	Effect of acidity 1% aqueous solutions of Co and Ni with 10% HCl in the ratio 1:1:1 by volume.	Co (0.31-0.0) – Ni (0.93-0.89)	Presence of acid in the sample makes the detection of Ni difficult
(b)	Effect of alkalinity 1%aqueous solutions of Co and Ni with 1M NH_4OH in the ratio 1:1:1 by volume	Co (0-0.0) – Ni (0.99-0.93)	Blue coloured cobalt solution turned golden yellow and green coloured Ni solution turned blue by the addition of 1M NH_4OH
(c)	Effect of surfactants 1% solutions of Co and Ni with 0.5% aqueous surfactant solution in 1:1:1 ratio by volume		
	(i) SDS	Co (0.18-0.0) – Ni (0.99-0.88)	Co gave elongated spots instead of circular spots in the presence of surfactants
	(ii) CTAB	Co (0.23-0.0) – Ni (0.98-0.79)	
(d)	1% solutions of Co and Ni with 1% aqueous solutions of SDS or CTAB in the ratio		Higher concentration of surfactant results in tailed spots for cobalt and the separation of Ni from Co is very poor
	(i) 1:1:1 v/v	Co(0.90-0.0)[a] - Ni(0.99-0.88)[a] Co(0.89-0.0)[b] - Ni(0.99-0.90)[b]	
	(ii) 1:1:2 v/v	Co(0.90-0.0)[a] - Ni(0.98-0.88)[a] Co(0.89-0.0)[b] - Ni(0.98-0.88)[b]	

All readings are taken as average of three observations. a-Results with SDS, b-Results with CTAB

[illegible] is linearly dependent on concentration of Co^{++} in the range 49-345 µg. The maximum recovery of cobalt after TLC separation from Ni^{++} was 92% and the standard deviation was 0.0432.

0.21

Presence of higher concentration of surfactants adversely affect the separation. A concentration of 1% aqueous SDS or CTAB in the sample gave tailed spot for cobalt ($R_F \geq 0.45$) and hindered its separation from nickel. However, the separation could be safely achieved if the concentration of added surfactant in the samples is kept below 1%.

Another important aspect of the present study is the microgram level separation of cobalt from nickel after pre-concentration of metal ions by precipitation with ammonium sulphide. The results were satisfactory and the developed method can be used for the separation of cobalt and nickel from water samples at ppm levels. For quantitative spectrophotometric determination a recovery curve for cobalt was constructed (Fig. 3.1) using optimum conditions described in the procedure. The absorbance is linearly dependent on concentration of Co^{++} in the range 49-345 µg. The maximum recovery of cobalt after TLC separation from Ni^{++} was 92% and the standard deviation was 0.0432.

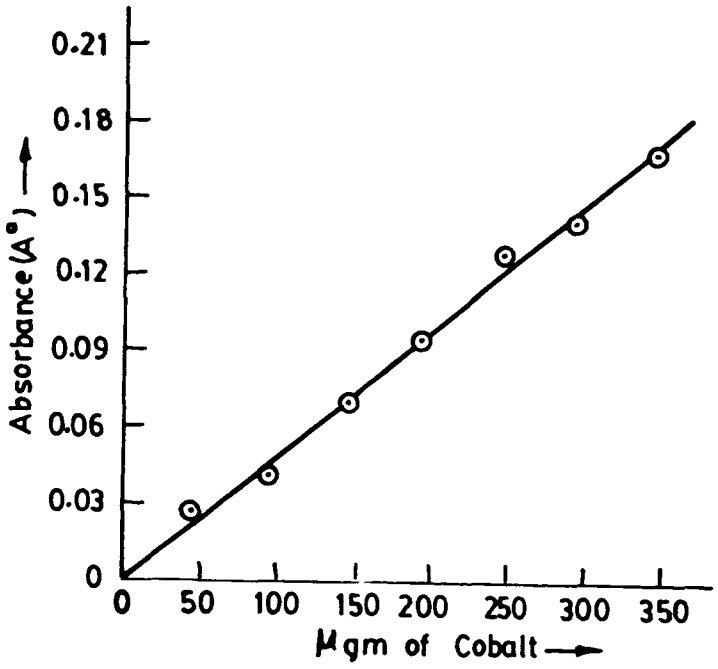

Fig.3.1: Recovery Curve for Cobalt.

Table 3.2: TLC Methods Used for the Separation of Nickel from Cobalt

S.No.	Stationary phase	Mobile phase	ΔR_F	Reference
1.	Maize starch	Butanol-pyridine-diethylaniline - 5N HCl (5:1:2:2)	0.17	21
2.	Cellulose	Acetone - Conc. HCl - H_2O (86:8:70)	0.24	22
3.	Silica gel impregnated with 0.1M pyrazole	8N HCl	0.35	23
4.	Silica gel G	Formic acid-propanol-2-acetone or 1,4-dioxane in various proportions	0.48	24*
5.	Stannic arsenate gel-silica gel (10:1) impregnated with 0.2M TBP	1M Potassium thiocyanate	0.91	Present Study

* Mutual separation of nickel and cobalt as their chlorosulphate complexes

ΔR_F = Difference between R_F values of Ni and Co.

The highest ΔR_F value obtained for the separation of nickel from cobalt by present method is indicative of well separated spots as components from their mixture (Table 3.2). Thus, the proposed method is the best available TLC method for resolving a mixture containing nickel and cobalt.

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CHAPTER IV

MICELLAR TLC SEPARATION OF HEAVY METAL CATIONS

4.1 INTRODUCTION

The micellar liquid chromatography (MLC) is currently enjoying popularity over other liquid chromatographic methods because of its unique advantages such as capability of simultaneous separation of ionic and nonionic compounds, faster analysis, and higher detection sensitivity and selectivity. The most fascinating feature of micellar systems is their dual hydrophobic and hydrophilic character which provide electrostatic and hydrophobic sites of interaction in the aqueous mobile phase resulting in unique separation possibilities of ionogenic and non-ionic solutes. As a result, micellar mobile phases have been extensively used in the reversed-phase chromatographic separation of various organic compounds. On the contrary, the use of micellar mobile phases in inorganic chromatography has been limited. The efficiency of mobile phases in the separation of cations (1,2) and anions (3,4) have been reported by T. Okada. Mullins and Kirkbright (5) have used MLC as an alternative to ion chromatography for the separation of several inorganic anions using a cationic micellar eluent. Kirkman et al. (6) have used a variety of micellar eluents to examine the chromatographic behaviour of ionic, non-ionic, chelated and organometallic metal species.

As much as micellar mobile phases have to offer to enhance selectivity, they suffer from a serious loss of efficiency when compared to traditional hydro-organic mobile phases. It has been reported by Dorsey et al. (7) that the addition of small concentration of different organic solvents to micellar mobile phases improves efficiencies by reducing the adsorbed amount of emulsifier (surfactant). The reasons for the occurrence of this unique phenomenon in MLC was attributed to the existence of the competing equilibria in MLC and the influence of micelles on the role of organic modifiers. Khaledi et al. have observed simultaneous enhancement of separation selectivity and solvent strength in MLC using hybrid eluents of micellar - organic solvents for different

groups of ionic and non-ionic compounds and both for cationic and anionic micellar mobile phases (8).

From literature, use of both normal and reversed-phase micelles as mobile phases in HPLC has been extensive but surfactant-mediated systems have just been touched in thin layer chromatography of inorganics (9-11). However, none of these studies refers to micellar TLC separations of heavy metal cations. A water-in-oil (w/o) microemulsion, consisting of sodium dodecyl sulphate/pentanol/water/heptane, has been used as mobile phase for identification and separation of anions on a variety of layers (9). Silica gel layers impregnated with cationic, anionic and non-ionic surfactants have been utilized for the separation of piperidinedithiocarbamate complexes of Pb, Cu, Fe and Cd using mono- and two-component organic solvents as mobile phases (10). Co(III)-1-(2-pyridylazo)-2-naphthyl complexes have been resolved on polyamide layers using a mixture of 6.4% sodium dodecyl sulphate, 10% triton X 100 and acetic acid - sodium acetate buffer (pH 4) in 5:8:3 ratio as mobile phase (11).

The present study was, therefore, undertaken to examine the migration behaviour of heavy metal cations on cellulose layers using aqueous micellar, hydro-organic and water-organic-surfactant mobile phases. Cellulose was selected because it being an organic polymer has been most useful for separating hydrophilic compounds such as amino acids and inorganic ions.

4.2 EXPERIMENTAL

Apparatus : A TLC apparatus (Toshniwal, India) was used to prepare cellulose layers (0.25mm) on 20×3cm glass plates. Glass jars (24×6cm) and an Elico pH meter were used for pH measurements. Spectrophotometric determination was done by an Elico Mini spec SL 171 spectrophotometer.

Chemicals and Reagents : Specially pure sodium dodecyl sulphate (SDS) from BDH, India; N-cetyl-N, N, N-trimethylammonium bromide (CTAB) from Romali, India; polyoxyethylene dodecyl ether (Brij-35) from Loba Chemie, India; polyoxyethylene (2) sorbitan monolaurate (Tween-20), microcrystalline cellulose, dimethylsulphoxide (DMSO), dimethylformamide (DMF) and acetone were all from CDH, India. All other Chemicals used were of analar grade.

Metal Ions Studied : Chlorides or nitrates of Ni^{2+}, Co^{2+}, UO_2^{2+}, VO^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Tl^{+}, Bi^{3+}, Hg^{2+}, Fe^{3+} and copper sulphate were from CDH, India and were of analytical reagent grade. 1% test solutions of these metal ions were prepared in double distilled water.

Detection : Ni^{2+} and Co^{2+} spots were detected with 1% alcoholic dimethylglyoxime solution while Fe^{3+}, Cu^{2+}, UO_2^{2+} and VO^{2+} were detected with 1% aqueous potassium ferrocyanide. 0.05% fresh dithizone solution in chloroform was used to detect Zn^{2+}, Cd^{2+}, Pb^{2+}, Tl^{+} and Ag^{+}.

Solvent Systems : The mobile phases used for development were :

No.	Composition
(a) Aq. surfactant solution	
M_1	Brij-35 (0.001, 0.1, 1, 3, 5, and 30%)
M_2	Tween-20 (1%)
M_3	CTAB (1 and 3%)
M_4	SDS (1 and 3%)
M_5	Triton X 100 (0, 0.2, 0.5, 1 and 3%)
M_6	1% Brij-35 - 1% CTAB (1:1 v/v)
M_7	1% Brij-35 - 1% SDS (1:1 v/v)
(b) Aq. surfactants + organic solvent	
M_8	0.001% Brij-35-acetone (1:1, 1:9, 9:1, v/v)
M_9	1% Brij-35-acetone (1:1, 1:9, 9:1, v/v)

M_{10} - 5% Brij-35-1, 4-dioxane (1:1 v/v)

M_{11} - 3% Brij-35-DMSO (1:1, 2:1, 7:3, 9:1 v/v)

M_{12} - 3% Brij-35-DMSO-acetone (8:1:1 v/v)

M_{13} - 3% Brij-35-DMSO-formic acid (8:1:1 v/v)

M_{14} - 3% Brij-35 - DMF (1:1, 2:1, 7:3, 9:1 v/v)

M_{15} - 3% Brij-35 - acetone (1:1, 2:1, 7:3, 9:1 v/v)

M_{16} - 3% CTAB-acetone (1:1, 2:1, 7:3, 9:1 v/v)

M_{17} - 3% SDS-acetone (1:1, 2:1, 7:3, 9:1 v/v)

M_{18} - 3% Brij-35 - methanol (1:1, 9:1, 1:9 v/v)

M_{19} - 3% Brij-35 - propanol (9:1 v/v)

M_{20} - 3% Brij-35 - ethylmethylketone (9:1 v/v)

M_{21} - 3% Brij-35 - 1, 4-dioxane (1:1, 2:1, 7:3, 9:1 v/v)

M_{22} - 0.01% Brij-35-acetone (1:1 v/v)

M_{23} - 0.1% Brij-35-acetone (9:1 v/v)

(c) Aq. surfactants + aq. inorganic salt

M_{24} - 1% Brij-35-ammonium acetate (1:1)

M_{25} - 1% Brij-35-citric acid (1:1)

M_{26} - 30% Brij-35-KSCN (1:1)

M_{27} - 1% Brij-35-3% NH_4SCN (1:1 v/v)

(d) Aq. surfactant + organic solvent + aq. inorganic salt

M_{28} - 30% Brij-35-acetone-KSCN (1:1:1)

M_{29} - 3% Brij-35-DMSO-ammonia (8:1:1 v/v)

(e) Organic solvents

M_{30} - 1, 4-dioxane

M_{31} - DMSO

M_{32} - DMF

(f) Hydro-organic solvents

M_{33} - Water - DMSO (9:1 v/v)

M_{34} - Water-acetone (9:1 v/v)

CHROMATOGRAPHY

Preparation of TLC Plates : A homogeneous slurry of the stationary phase microcrystalline cellulose (20g) and double-distilled water (60ml) was prepared by constant shaking for 5 min. The slurry was coated immediately onto 20×3 cm^2 plates, as a 0.25mm layer, by means of a Toshniwal, India, TLC applicator. Plates were dried at room temperature and activated at 50±2°C for 1 h in an electrically controlled oven. After activation the plates were cooled at room temperature and stored in a closed chamber at room temperature before use. No binder was added during the preparation of the plates.

PROCEDURE

Chromatography was performed in 24×6×6 cm^3 glass jars. Sample solutions (10 µL) were applied to the plate on a line marked at 3 cm from one edge, using lambda pipettes and left to dry in air . Ascending development in various mobile phases was performed to a distance of 10 cm from the point of application. After development, the plates were dried at room temperature and the positions of the metal ions were revealed as clearly observable spots by spraying with the respective detection reagents. For the separation of metals, samples (1%, 10µL) of each metal was mixed together and 10 µL of the resultant mixture was applied on the plates and the chromatography was performed as described above. The R_F values of the separated spots were determined.

Quantitative Determination of Uranium by Spectrophotometry

5mL of arsenazo (III) reagent (0.05% in 0.1M HCl, pH ~ 2.5) was added to a solution of aqueous uranyl nitrate (containing 11.25 - 118.53 µg uranium). The contents were diluted with 15mL distilled water and the solution was kept undisturbed for 2 hours to ensure complete colour development. Absorbance spectra of this solution was measured against reagent blank between 480 and 680nm. Maximum

absorbance (λ_{max}) was noticed at 650nm. The stability of colour produced with uranium was observed at regular intervals of 2 hours for a period of 24 hours and the colour was found stable during this period.

This spectrophotometric method was used to determine uranium after chromatographic separation from other metal ions viz. Fe and Hg. Different volumes (2.5 - 25μL) of uranyl nitrate solution containing 11.85 - 118.53 μg uranium were mixed with a solution containing iron and mercuric chloride (10μg each). The 10μL of resultant mixture (uranium + iron + mercury) was loaded on a set of TLC plates (working plates). A second set of plates (pilot plates) was also loaded with exactly the same amount of UO_2^{2+}, Fe^{3+} and Hg^{2+} as on the working plates. The plates were allowed to dry at room temperature and both sets of plates were developed simultaneously with the mobile phase (3% Brij + DMSO 9:1, v/v). The exact position of uranium spot on the pilot plate was identified by detecting it with potassium ferrocyanide. The corresponding portion for uranium on the semi-dried working plate was marked on the basis of position identified on pilot plate for UO_2^{2+}, the area of adsorbent corresponding to UO_2^{2+}on working plate was scraped into a clean beaker and UO_2^{2+} was extracted with 1M HCl (~ 5mL). The contents were well stirred and the adsorbent was filtered out with subsequent washing of adsorbent with distilled water. The filtrate collected in a conical flask was evaporated to dryness for the removal of HCl. The residue so obtained was mixed with 5mL of 0.05% aqueous acidic arsenazo (III). The bluish-green coloured complex so formed was then diluted to 15mL with distilled water, the absorbance at λ=650nm was measured against reagent blank and the absorbance was plotted against the concentration of UO_2^{2+} to sketch the standard calibration curve which was used to find out the percentage recovery of uranium after its chromatographic separation from iron and mercury.

4.3 RESULTS AND DISCUSSION

The preliminary chromatographic studies of metal ions with 1% aqueous surfactant solutions reveal that (i) SDS, CTAB and Tween-20 are unsuitable for TLC separation of metal ions because of the difficulty of detection and the formation of tailed spots and (ii) all the metal ions were well detected with Triton and Brij. However, badly tailed spots were produced in the case of Triton whereas relatively less tailed spots were obtained with Brij.

In order to find out the optimum concentration of surfactants, different aqueous concentrations of Triton (0.2-3%) and Brij (0.001 - 5%) were used as mobile phase. At all concentrations, better separation possibilities were found with Brij compared to Triton. Hence, Brij was selected for detailed studies.

The results obtained with entire range of Brij concentration (0.001 - 5%) are summarized below.

(i) At very low surfactant concentration (0.001%) which is below the CMC (0.012%) of Brij-35, where the surfactant remains in the form of monomers, all metal ions tailed ($R_L - R_T > 0.3$) except Bi^{3+} ($R_F = 0.9$), Hg^{2+} ($R_F = 0.7$) and UO_2^{2+} ($R_F = 0.1$).

(ii) At surfactant concentration (0.01%) which is very close to CMC value, less tailed spots with increased compactness were realized.

(iii) At higher concentrations (0.1-5%), which is well above the CMC vlaue of surfactant the migration behviour of most metal ions do not appreciably change and the results were more or less similar to those obtained at surfactant concentration of 0.01%. The development time (~ 2min for 5cm ascent) was almost the same at all concentrations of surfactant.

It seems that various types of structures of surfactant molecules

which are simply generated by increasing the concentration of surfactant in water with a concomitant change in the size of the aggregates (12) do not offer substantial influence on the mobility of the metal ions. The spherical micelles formed near the CMC becomes cylindrical which may be converted into a hexagonal packing of surfactant molecules to lamellar structures by increasing the concentration of surfactant in aqueous medium. In general, the whole concentration range (0.001 - 5%) of Brij could not provide satisfactory media for the separation of heavy metal cations due to considerable tailing. This problem arises probably duet to slow kinetics in micellar partitioning as observed by several other workers who realized peak broadening (8, 13, 14). Thus, micellar mobile phases were not found useful for the separation of heavy metal cations. With the aim of improving separation efficiency of micellar mobile phases, we add ionic additives (citric acid, ammonium acetate, potassium or ammonium thiocyanate) to aqueous solution of Brij-35 ($M_{24\text{-}27}$) and the resulted mobile phases were used as developers. The increased mobility (R_F = 0.8) for all metal ions coupled with enhanced compactness was noticed. Further, these mobile phases have no practical utility as none of the metal ions could be separated from accompanying metals due to non-differential migration.

Mixed micelles, obtained on mixing 1% each of SDS or CTAB with 1% Brij-35 in 1:1 ratio, by volume were transparent solutions. These mixed micelles were used as mobile phase for TLC of metal ions. Compared to CTAB, SDS mixed micelles proved better in terms of better detection and compact spot formation for Zn, Cd, Pb, Tl, Bi, Hg and Ag. However, due to identical migration behaviour, separation possibilities of metal ions could not be realized.

Many researchers have advocated for the improved efficiency of micellar systems in the presence of organic additives (alcohols, alkanes, diols and dipolar aprotic solvents) in reversed-phase liquid chromatog-

raphy (15). With this in mind, we selected DMF (polar liquid), MeOH (more polar protic solvent), acetone (aprotic and relatively non-polar solvent), and DMSO and dioxane (aprotic dipolar solvents) for examination of their effect on retention behaviour of heavy metal cations. These organic solvent were mixed with 3% aqueous Brij-35 solution in different volume ratio (M_{8-23}, M_{29}, M_{33-34}). The results obtained with these hybrid mobile phases (micelles-water-organic solvent) are summarized below in order to understand the effect of adding organic solvents to micellar mobile phases on the mobility of heavy metal ions.

(i) With micellar mobile phases containing DMF (M_{14}), the presence of organic solvent (10-50%) in the micellar eluent did not exert any significant effect on the mobility of metal ions.

(ii) In the presence of methanol, all metal ions produce badly tailed spots except Hg^{2+} (R_F = 0.87) in the concentration range of 10-90%.

(iii) Almost identical results were obtained with solvent systems containing DMSO and dioxane. Both organic solvents (DMSO and dioxane) being aprotic dipolar behave in an identical fashion in micellar systems containing 10-50% DMSO or dioxane to influence the mobility of metal ions. All metal ions have R_F value higher than 0.50 except Fe^{3+} and UO_2^{2+} where R_F values are 0.15 and 0.40 respectively. The mobile phase containing 10% DMSO and 90% micellar eluent was found more useful for better detection and separation. DMSO with hard oxygen and soft sulfur is a strong solvating agent for cations in preference to anions. It also decreases the dielectric constant leading to the formation of non-dissociated metal complexes. DMSO with its unique properties such as high dielectric constant (48.9 at 20°C), tendency to form complexes with many metal ions and containing no ionizable protons has received attention of researchers for its use as solvent

in ion-exchange and thin layer chromatographic separations of metal ions (16-19).

(iv) All the metal ions remained at the point of application on cellulose layers developed with any of the pure organic solvents e.g. methanol, DMSO, dioxane, acetone etc.

(v) Organic solvent - water (or hydro-organic) systems produce badly tailed spots of almost all metal ions on cellulose layers. These results are in consonance of our previous observations (16) where metal ions gave badly tailed spots on silica gel layers developed with water-DMSO and water-acetone systems.

(vi) Micelle - acetone-water system was found the best for separation of metal ions. Acetone with low dielectric constant favours the formation of non-dissociated metal complexes. Acetone does not solvate the ions and it has the tendency to suppress hydrolysis of metal ions to give more compact spots. The highly compact spots with maximum separation possibilities were achieved with micellar mobile phases containing 10% acetone with 3% Brij (Fig. 4.1). Fig. 4.1 reveals the effect of change in concentration of Brij at constant concentration of acetone. Most of the metal ions produce tailed spots in micellar eluents containing 10% acetone and upto 1% Brij in 1:9 ratio. For better detection possibilities with identical R_F values one can switch over to ethyl methyl ketone from acetone.

It appears that non-polar organic solvents (ethyl methyl ketone and acetone) are better eluents in combination with non-ionic micellar systems (i.e. Brij-35). Compared to more polar organic solvents (MeOH, DMF). The non-polar organic solvents are associated with the core of micelle whereas polar organic solvent are found in the outer regions of the core (20). Thus, the position of organic modifier in the micelle

influences the retention behaviour of metal ions. Slightly higher mobility of most of metal ions as noticed by us in methanol containing micellar systems compared to the mobility in acetone containing micellar mobile phases is probably due to faster partitioning of metal ions in outer region of micelles containing methanol.

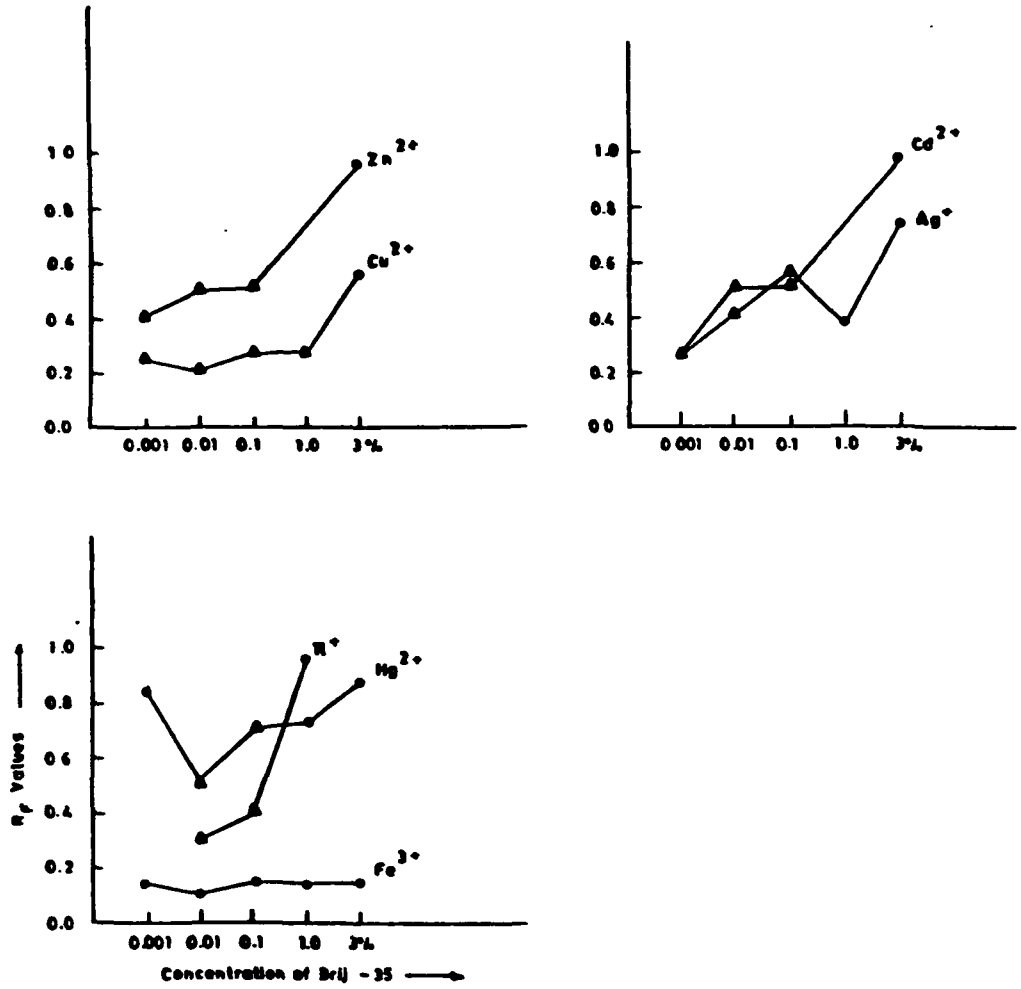

Fig. 4.1 - Effect of Concentration of Brij -35 Micelle with Fixed Concentration of Acetone on the Mobility of Heavy Metal Cations

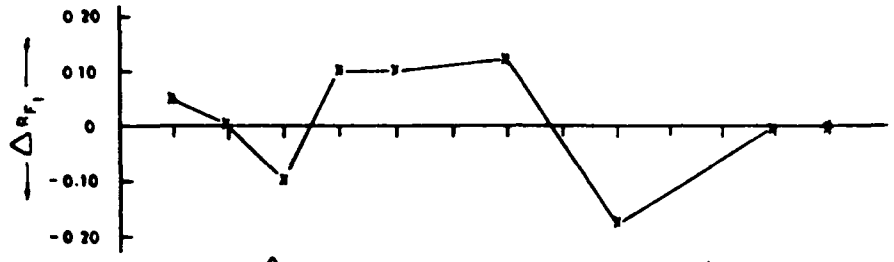

Fig. 2a. ΔR_{F_1} = R_F in 1% Brij + acetone (9:1) - R_F in 0.001% Brij + acetone (9:1)

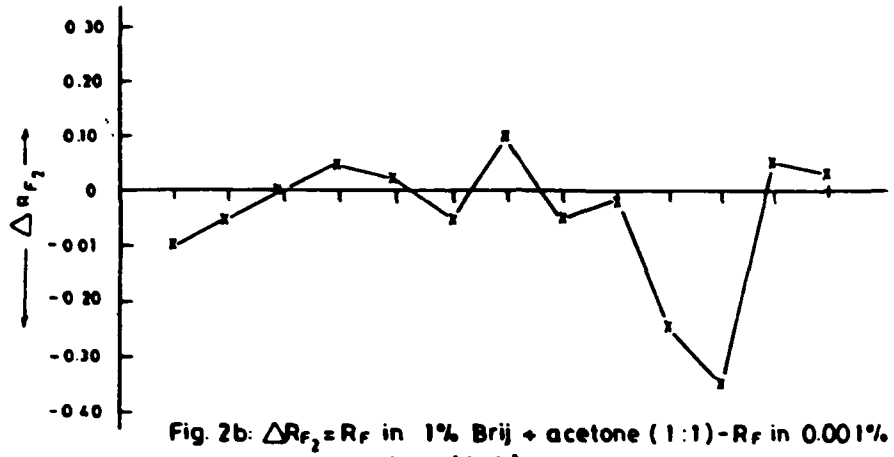

Fig. 2b: ΔR_{F_2} = R_F in 1% Brij + acetone (1:1) - R_F in 0.001% Brij + acetone (1:1)

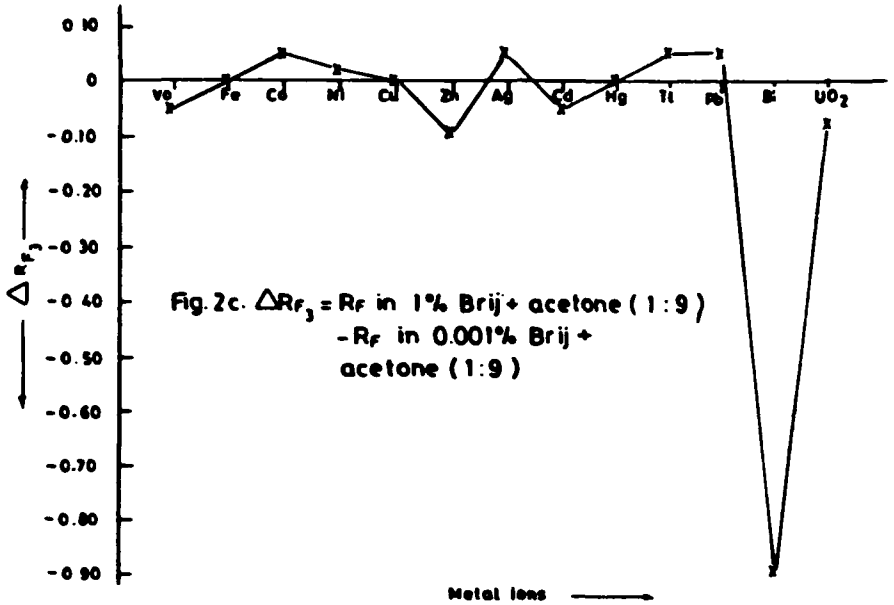

Fig. 2c. ΔR_{F_3} = R_F in 1% Brij + acetone (1:9) - R_F in 0.001% Brij + acetone (1:9)

Fig 4.2 - Plot of ΔR_F Vs Metal ions

In Fig. 4.2, ΔR_F values [(R_F in 1% Brij + acetone) – (R_F in 0.001% Brij + acetone) in 9:1 (Fig 4.2a), 1:1 (Fig. 4.2b) and 1:9 (Fig. 4.2c)] were plotted against metal ions taken in the order of their increasing atomic number. It is clear from the figure that the mobility of Ni, Co, Cu, Ag and Hg is most effected at 10% acetone in different concentrations of Brij (Fig. 4.2a) as indicative by negative and positive values of ΔR_F . The difference in mobility of metal ions decreases on the increase of volume of acetone in micellar mobile phase (Fig. 4.2b and c). At 50% acetone, V, Ag, Tl and Pb show differential migration and these metals migrate faster in eluent containing 0.001% Brij, giving negative ΔR_F values. Contrary to this, lower mobility for Ag is noticed in this system (+ve ΔR_F value). At 90% acetone, except Bi and Zn all the metal ions studied show almost identical mobility in both micellar mediated systems containing 0.001% and 1% Brij. Both metal ions show higher mobility in mobile phases containing lower concentration of micelles. From these results, it may be concluded that migration behaviour of metal ions is controlled by the concentration of Brij at constant concentration of acetone and vice versa.

The separations achieved experimentally with different micellar mobile phases on cellulose layers have been listed in Table 4.1. These separation possibilities arise as a result of tendency of Brij and DMSO to form metal complexes, selective partitioning of metal ions/complexes into micellar eluent, polar nature of cellulose exchanger, weaker interaction of acetone with metal ions, simultaneous change in surface tension and the strength of surfactant mediated hydro-organic mobile phases with the simultaneous change in concentrations of surfactant and organic solvents. The non-ionic surfactants containing poly (oxyetylene) chains have been considered as neutral ionophores which are with capable to react with some metal ions to form charged complexes (21).

Table 4.1 : Experimentally Achieved Separations on Cellulose With Various Mobile Phase

Mobile Phase	Separations (R_F)
1. 1% Brij	Fe^{3+}(0.15) - Ag^{+}(0.80)
2. 3% Brij-DMSO (9:1)	Hg^{2+}(0.95) - UO_2^{2+}(0.45) - Fe^{3+}(0.12)
	Fe^{3+}(0.10) - Cu^{2+}(0.47)
3. 3% Brij-DMSO-Acetone (8:1:1)	Hg^{2+}(0.95) - UO_2^{2+}(0.50) - Fe^{3+}(0.12)
4. Triton (0.5%)	Hg^{2+}(0.90) - Co^{2+}(0.50) - Fe^{3+}(0.10)
	Hg^{2+}(0.85) - Ni^{2+}(0.40) - UO_2^{2+}(0.15)
5. 3% Brij-DMF (7:3)	Fe^{3+}(0.10) - Cu^{2+}(0.45) - Hg^{2+}(0.90)
6. 3% Brij-Acetone (7:3)	Fe^{3+}(0.10) - Ni^{2+}(0.57) - Hg^{2+}(0.99)
	Fe^{3+}(0.10) - Ni^{2+}(0.55) - Bi^{3+}(0.95)
7. 3% Brij-Acetone (9:1)	Fe^{3+}(0.10) - Cu^{2+}(0.50) - Zn^{2+}(0.85)
	Fe^{3+}(0.10) - Cu^{2+}(0.52) - Cd^{2+}(0.85)
	Fe^{3+}(0.10) - Cu^{2+}(0.47) - Tl^{+}(0.90)
	Fe^{3+}(0.10) - Cu^{2+}(0.50) - Hg^{2+}(0.90)

In addition to qualitative analyses, quantitative determination of analyte is usually required in TLC. For the same reason, we have developed a spectrophotometric method for the quantitative determination of UO_2^{2+} with its preliminary separation from Fe^{3+} and Hg^{2+} . The separation of UO_2^{2+} from Fe^{3+} is important because both the metal ions produce ferrocyanide complexes with potassium ferrocyanide (22) and hence Fe^{3+} interferes in the detection and determination of UO_2^{2+} with potassium ferrocyanide.

Table 4.2 : Sepectrophotometric Determination of Uranium after TLC Separation from Fe^{3+} and Hg^{2+}

Amount loaded(μg)	Amount Recovery (μg)	% Error	% Recovery
11.85	9.46	20.16	79.88
23.70	19.51	17.67	82.34
47.41	43.47	8.31	91.70
71.12	66.07	7.10	92.91
94.82	84.97	10.38	89.62
118.53	106.89	9.82	90.18

The results of spectrophotometric determination of uranyl nitrate are given in Table 4.2. The absorbance is linearly dependent on concentration in the range 11.85 - 118.53 μg of UO_2^{2+} in the solution. The maximum recovery of UO_2^{2+} after TLC separation from iron and mercury is 93%.

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CHAPTER V

DETECTION, IDENTIFICATION AND SEPARATION OF HEAVY METALS ON MIXED LAYERS PREPARED FROM MIXTURE OF SILICA GEL AND INORGANIC ION-EXCHANGERS

5.0a STUDIES ON SILICA GEL-SUPPORTED STANNIC ARSENOSILICATE LAYERS

5.1a INTRODUCTION

A variety of coating materials are available as stationary phase for thin layer chromatography (TLC) of inorganics (1). Silica gel and alumina containing hydroxyl groups have been the more frequently used layer materials. However, the separation of cations on silica gel or alumina has not always been satisfactory as many cations remained grouped together on these adsorbents. Ion-exchange resins in particle size of 40-80 μm have also been found suitable for preparing thin layer plates.

Mixed sorbent layers have been used by various workers to increase resolution of certain samples compared to that obtained on the separated phases. Binary layers prepared from mixtures of silica gel and alumina, cellulose, polyamide or kieselguhr have been used to achieve enhanced resolution of components. The use of mixed layers comprising of silica gel and inorganic ion-exchange gel layer has been found (2) advantageous for the separation of ionic species because of the more predominent role of mixed layer as an ion-exchanger compared to its adsorption behaviour. It is therefore, amenable to develop new layer materials by combining the ion-exchange properties of synthetic inorganic ion-exchange gels with adsorptive properties of silica gel.

This report describes the use of silica gel - supported stannic arsenosilicate gel as stationary phase for detection and selective separation of certain heavy metals. Stannic arsenosilicate was selected because of its good ion-exchange properties (3, 4). Stannic arsenosilicate, a cation exchanger has been synthesized, characterized and utilized for the separation of metal ions by column chramatography (3). However, its use in TLC is lacking.

5.2a EXPERIMENTAL

Reagents : Anhydrous stannic chloride, sodium arsenate, formic acid and sodium formate were of CDH, India. Sodium meta silicate from Loba Chemie Pvt. Ltd. and tributylamine (TBA) of Fluka. All other reagents were of analytical reagent grade.

Test Solutions and Detection Reagents : The test solutions were all 1% of their metal chlorides, nitrates or sulphates. Potassium ferrocyanide (1%) was used for the detection of Fe^{3+}, Cu^{2+} and 01.% dithizone in carbon tetrachloride was used to detect Zn^{2+} and Cd^{2+}. Ni^{2+} and Co^{2+} were detected with 1% alcoholic dimethylglyoxime solution and 1% ammonium sulphide solution was used to detect Pb^{2+}, $Ag.^{+}$, Tl^{+}, Bi^{3+} and Hg^{2+}.

SYNTHESIS OF ION-EXCHANGER GEL

0.1 M Aqueous solutions of sodium arsenate, sodium silicate and stannic chloride were used for the synthesis of stannic arsenosilicate ion exchanger. These three equimolar solutions were mixed in various volume ratios but the maximum gel formation was obtained with the volume ratio of 1:1:1. The pH of the gel was maintained at 1 with HNO_3. The gel was kept for 24 hours at room temperature and thoroughly washed with demineralized water to remove excess reagents before use.

CHROMATOGRAPHY

Stationary Phases

(a) Plain Silica gel G (S_1): Thin layer of 0.25 mm thickness of silica gel G (Merck, India) was coated on 20 x 30 cm glass plates with the help of an applicator (Toshniwal, India). After complete drying at room temerature the plates were activated at 100 ± 5°C for 1 h in an electrically controlled oven. The activated plates were kept in a closed chamber at room temperature until used.

(b) Mixed Silica gel G- stannic arsenosilicate gel (S_2) : Silica gel G (20 gm) was added to 20 gm of stannic arsenosilicate ion-exchanger gel and the mixture was triturated well in a mortar to prepare a homogenous slurry which was spread onto glass plates.

(c) Impregnated layer (S_3–S_5) : The mixed silica gel G - stannic arsenosilicate gel plates were impregnated with different concentrations of tributylamine in methanol

S_3 - 10% TBA impregnation on S_2
S_4 - 15% TBA impregnation on S_2
S_5 - 20% TBA impregnation on S_2

Mobile Phase

M_2 - IM Formic acid (FA)
M_2 - 1M Sodium formate (SF)
M_3 - 1M FA - 1M SF (4:1)
M_4 - 1M FA - 1M SF (2:3)
M_5 - 1M FA - 1M SF (3:2)
M_6 - 1M FA - 1M SF (1:4)
M_7 - 1M FA - 1M SF (1:1)
M_8 - 10% TBA in methanol
M_9 - 15% TBA in methanol.
M_{10} - 20% TBA in methanol.

PROCEDURE

A micropipette was used to spot the sample solutions (3-5 µl) of metals on the activated TLC plates. The spots were dried at room temperature before development. The TLC plates were developed in various solvent systems mentioned above by the ascending technique keeping the solvent run to 10 cm in all cases. After development, the plates were air dried, and the metal ions were detected using the ap-

propriate chromogenic reagent. Retardation factor (R_F) values were calculated from the R_F values of leading (R_L) and trailing (R_T) fronts. The limits of detection of metals were determined by spotting S_2 plates with 0.01 ml of standard solution followed by development with M_3 and the detection of metal spots using appropriate spraying reagent. The process was repeated with successive reduction of concentration of metal ions until no detection was possible. The minimum amount of detectable salt in solution was taken as its detection limit. With the same chromatographic system (S_2-M_3), the effect of metal ions concentration on their R_F values was examined in the case of Ag^+-Zn^{2+} and Pb^{2+}-Ni^{2+} separations. For this purpose, the loading amount of one of the components (eg. Ag^+ or Pb^{2+}) was kept constant (10μg) and the amount of another component (e.g. Zn^{2+} or Ni^{2+}) was varied (40-100 μg) in the mixture of two-component sample 0.01 mL of the synthetic mixture of sample was applied on TLC plate and the R_F values of the resolved spots were determined. The increase in loading amount of metal ion (Zn^{2+} or Ni^{2+}, 40-100 μg) results in the slight decrease in the R_F value without hampering the separation of Zn^{2+} and Ni^{2+} from Ag^+ and Pb^{2+} respectively.

5.3a RESULTS AND DISCUSSION

The folloiwng points emerged out from this study.

(a) Stannic arsenosilicate gel in the wet form cannot be used as a layer material even in the presence of binder (starch or polyvinyl alcohol). We tried to coat the ion-exchanger gel in the absence of binder as well as in the presence of 5-10% starch or polyvinyl alcohol on glass plates but no desired layer formation was achieved. However, good quality plates coated with a mixture consisting of silica gel G and stannic arsenosilicate gel in 1:1 ratio by weight were easily prepared in our laboratory. The idea of preparing

TLC plate by coating dried ion-exchanger was abandoned because of the high cost of end product and the requirement of large quantity of ion-exchanger. On the other hand the preparation of slurry of dried ion-exchanger for TLC was time consuming and tedious.

(b) Amongst stationary phases S_1-S_5, better separation possibilities were observed with S_3.

(c) Amongst solvent system M_1-M_{10}, best results in respect of spot detection, differential migration of metal ions and spot compactness were achieved with M_3.

(d) Better results were obtained with TBA as impregnant compared to its use a mobile phase.

(e) Formic acid containing mobile phases were found better solvent systems compared to TBA containing mobile phases.

(f) The decreasing order of mobility of metal ions on different stationary phases with M_3 was found as $S_1 > S_2 > S_3 > S_4 > S_5$. It shows that both ion-exchange and adsorption phenomena are operative to control the retention of metal ions.

The resuslts of this study are summarized in Fig. 5.1 and Tables 5.1, 5.2. Amongst unimpregnated layers (Fig. 5.1a) mixed layers are more selective for VO^{2+}, Ni^{2+}, Zn^{2+}, Tl^{+} and UO_2^{2+} (low R_F values) compared to plain silica gel layers (Fig. 5.1) as evident from positive vlaues of ΔR_{F1} (ΔR_{F1} = R_F on silica gel layer – R_F silica gel mixed with inorganic ion exchanger gel). Conversely, mixed layer is more selective to Bi^{3+}. The selectivity of mixed layers is further improved on impregnation with TBA as evident from Fig. 5.1b. The positive values of ΔR_{F2} (ΔR_{F2} = R_F on plain SG – R_F on mixed impregnated layer).

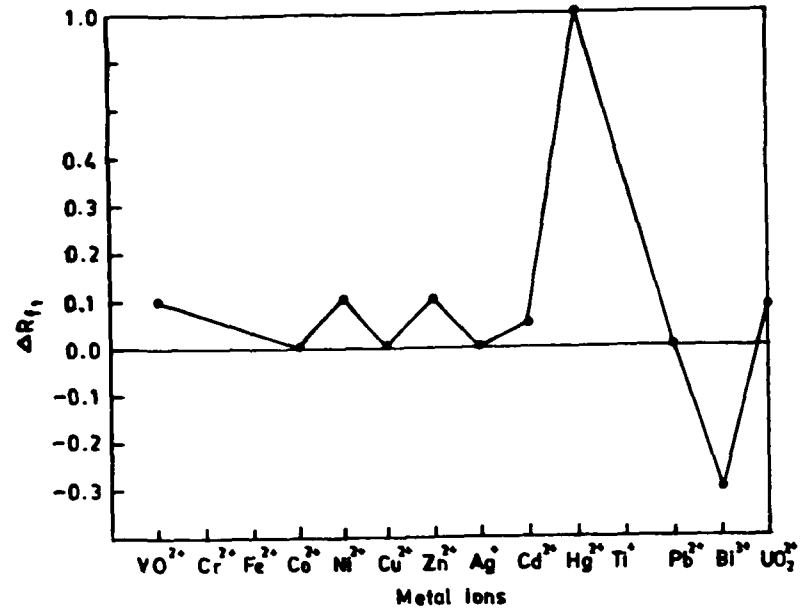

Fig.5.1(a): Plot of metal ions Vs ΔR_{f_1}

(ΔR_{f_1} = R_f Of metals on S_1 - R_f of metals on S_3)

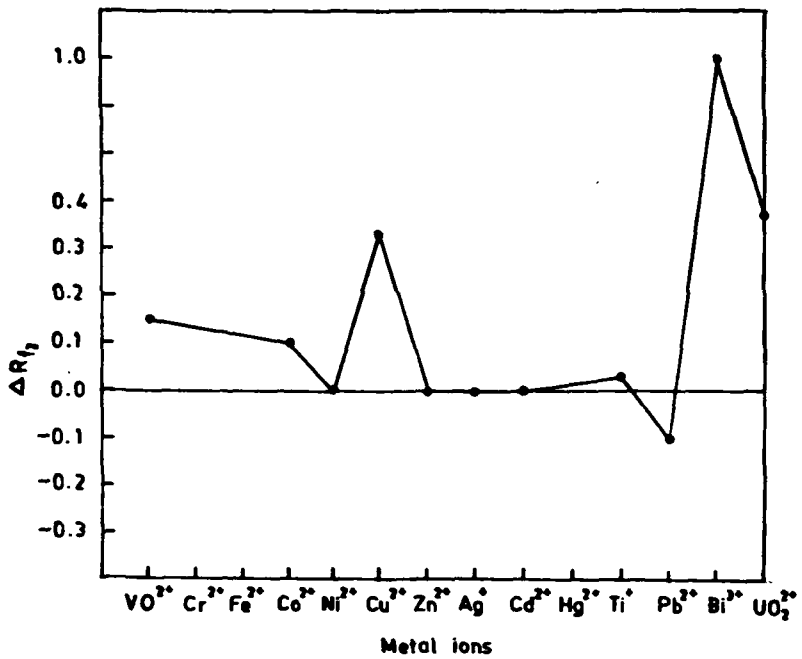

Fig.5.1(b): Plot of metal ions Vs ΔR_{f_2}

(ΔR_{f_2} = R_f of metals on S_2 - R_f of metals on S_3)

For most of the metal ions except Pb^{2+}, Ni^{2+}, Zn^{2+}, Ag^{+} and Cd^{2+} show that impregnated mixed layers are more selective for metal ions compared to silica gel or unimpregnated mixed layers. Certain metal ions (ΔR_{F1} or $\Delta R_{F2} = 0$) show the indentical selectivity on both the adsorbents taken for comparison. Thus, the mixed layers (impregnated and unimpregnated) can be utilized for selective separations of certain metal ions (Tables 5.1, 5.2). The sensitivity data (limits of detection) obtained for different metal ions and are given in parenthesis in μg are: Fe^{3+} (17.21), Cu^{2+} (7.96), Ni^{2+} (2.26), Co^{2+} (9.078), UO_2^{2+} (12.52), Cd^{2+} (12.26), Zn^{2+} (9.59), Ag^{+} (0.63), Pb^{2+} (3.12), Tl^{+} (7.67), Bi^{3+} (5.29) and Hg^{2+} (14.0).

Therefore, this newly developed sorbent phase, S_3 can be utilized as an inexpensive and highly selective layer material for the identification, detection and separation of certain heavy metals.

Table 5.1 : Separation of Metal Ions by TLC on Mixed Layers of Stannic Arsenosilicate - Silica Gel G in Various Mobile Phases

Mobile Phase	Separations (R_F)
M_1	$Ni^{2+}(1.0)$ - $Ag^{+}(0)$, $Ni^{2+}(1.0)$ - $Pb^{2+}(0)$, $Co^{2+}(1.0)$ - $Ag^{+}(0)$, $Co^{2+}(1.0)$ - $Pb^{2+}(0)$, $Bi^{3+}(1.0)$ - $Pb^{2+}(0)$, $Bi^{3+}(1.0)$ - $Pb^{2+}(0)$
M_2	$Co^{2+}(1.0)$ - $Ag^{+}(0)$, $Co^{2+}(1.0)$ - $Pb^{2+}(0)$, $Co^{2+}(1.0)$ - $Tl^{+}(0.42)$, $Bi^{3+}(0.90)$ - $Ag^{+}(0)$, $Bi^{3+}(0.90)$ - $Pb^{2+}(0)$, $Bi^{3+}(0.90)$ - $Tl^{+}(0.42)$
M_3	$Co^{2+}(1.0)$ - $Ag^{+}(0)$, $Ni^{2+}(0.90)$ - $Ag^{+}(0)$, $Cu^{2+}(0.90)$ - $Ag^{+}(0)$, $UO_2^{2+}(0.90)$ - $Ag^{+}(0)$, $Cd^{2+}(0.75)$ - $Ag^{+}(0)$, $Zn^{2+}(0.75)$ - $Ag^{+}(0)$, $Bi^{3+}(1.0)$ - $Ag^{+}(0)$, $Co^{2+}(1.0)$ - $Pb^{2+}(0)$, $Ni^{2+}(0.90)$ - $Pb^{2+}(0)$, $Cu^{2+}(0.90)$ - $Pb^{2+}(0)$, $UO_2^{2+}(0.90)$ - $Pb^{2+}(0)$, $Cd^{2+}(0.75)$ - $Pb^{2+}(0)$, $Zn^{2+}(0.75)$ - $Pb^{2+}(0)$, $Bi^{3+}(1.0)$ - $Pb^{2+}(0)$.
M_4	$Bi^{3+}(1.0)$ - $Fe^{3+}(0.15)$, $Bi^{3+}(1.0)$ - $Ag^{+}(0)$, $Bi^{3+}(1.0)$ - $Pb^{2+}(0.01)$, $Bi^{3+}(1.0)$ - $Tl^{+}(0.32)$
M_5	$Cu^{2+}(1.0)$ - $Ag^{+}(0)$, $Cu^{2+}(1.0)$ - $Pb^{2+}(0)$, $Cu^{2+}(1.0)$ - $Tl^{+}(0.3)$
M_6	$Cd^{2+}(1.0)$ - $Fe^{3+}(0.10)$, $Cd^{2+}(1.0)$ - $Ag^{+}(0)$, $Cd^{2+}(1.0)$ - $Pb^{2+}(0.10)$, $Cd^{2+}(1.0)$ - $Hg^{2+}(0)$, $Bi^{3+}(1.0)$ - $Fe^{3+}(0.10)$, $Bi^{3+}(1.0)$ - $Ag^{+}(0)$, $Bi^{3+}(1.0)$ - $Pb^{2+}(0.10)$, $Bi^{3+}(1.0)$ - $Ag^{+}(0)$, $UO_2^{2+}(0.80)$ - $Fe^{3+}(0.10)$, $UO_2^{2+}(0.80)$ - $Ag^{+}(0)$, $UO_2^{2+}(0.80)$ - $Pb^{2+}(0.10)$, $UO_2^{2+}(0.80)$ - $Hg^{2+}(0)$.

Table 5.2 :Separation of Metal Ions by TLC on Mixed Layers of Stannic Arsenosilicate - Silica Gel G Impregnated with Tributylamine in Different Solvent Systems.

Mobile Phase	Stationary Phase	Separations (R_F)
M_1	S_3	$Ni^{2+}(1.0)$ - $Fe^{3+}(0.05)$, $Ni^{2+}(1.0)$ - $UO_2^{2+}(0.15)$, $Ni^{2+}(1.0)$ - $Ag^{+}(0)$, $Ni^{2+}(1.0)$ - $Pb^{2+}(0)$, $Ni^{2+}(1.0)$ - $Tl^{+}(0.25)$, $Ni^{2+}(1.0)$ - $Bi^{3+}(0)$.
M_3		$Co^{2+}(0.90)$ - $Pb^{2+}(0.10)$, $Co^{2+}(0.90)$ - $Ag^{+}(0)$, $Co^{2+}(0.90)$ - $Bi^{3+}(0)$, $Co^{2+}(0.90)$ - $Hg^{2+}(0)$, $Ni^{2+}(0.90)$ - $Pb^{2+}(0.10)$, $Ni^{2+}(0.90)$ - $Ag^{+}(0)$, $Ni^{2+}(0.90)$ - $Bi^{3+}(0)$, $Ni^{2+}(0.90)$ - $Hg^{2+}(0)$
M_7	S_4	$Fe^{3+}(0.90)$ - $Ag^{+}(0)$, $Fe^{3+}(0.90)$ - $Pb^{2+}(0.12)$, $Fe^{3+}(0.90)$ - $Tl^{+}(0.25)$, $Fe^{3+}(0.90)$ - $Bi^{3+}(0)$, $Fe^{3+}(0.90)$ - $Hg^{2+}(0)$.

5.0b NORMAL-PHASE AND REVERSED - PHASE TLC WITH LAYERS OF SILICA - ZIRCONIUM TUNGSTOPHOSPHATE GELS

5.1b INTRODUCTION

In 1958, Winschester (5) first combined the favourable features of high- molecular weight extractants with a chromatographic technique and separated a number of rare earth elements using di (2-ethyl hexyl) phosphoric acid loaded on alumina as stationary phase and dilute HCl as the mobile phase. Since then, the technique of reversed - phase chromatography (or reversed-phase extraction chromatography) has become very popular. Several papers have been published (6-10) on reversed - phase thin layer chromatography (RPTLC) of metal ions using long - chain aliphatic amines, substituted quarternary ammonium salts, heterocyclic amines and neutral organophosphorous compounds as impregnants of the stationary phase. Solutions of strong monobasic acids or their alkali metal salts are generally selected as the mobile phase.

Tri-n-butyl phosphate (TBP), one of the most versatile extractants has received considerable attention in analytical separation chemistry because of its capability to extract most of the elements of the periodic table under suitable conditions of extraction. Since its first use of the separation of Th and V from impurities (11), TBP has been used extensively as extracant to accomplish analytical scale separations of antinides, lanthanides and Pt- group elements. However, its use for the separation of transition metals has been limited. From literature,TBP impregnated layers of silica gel, polyvinyl chloride and cellulose have been used to separate various metal ions (12-14). As far as we are aware, no work has been reported on the use of layers prepared from mixtures of inorganic ion-exchanger gel and silica gel in the presence

of TBP and crown ethers as impregnants or eluents in the analysis of transition metal ions.

The present study is an attempt to examine the use of silica-inorganic ion exchanger gel in RPTLC of certain metal ions. For this purpose, zirconium (IV) tungstophosphate ion exchanger in gel form was mixed with silica gel G. The resultant mixture was used as layer material after impregnation with TBP at different concentration levels to separate metal ions using HCl or formic acid containing solvent systems as eluents. Efforts were also made to explore the possible use of crown ethers as impregnants or as eluents in inorganic TLC.

5.2b EXPERIMENTAL

Materials : Zirconium oxychloride, sodium tungstate, orthophosphoric acid, tri-n-butyl phosphate and all other reagents were of analytical reagent grade of CDH, India. Benzo-15-crown-6 and dibenzo -18-crown-6 were of Aldrich, USA.

Test Solutions and Detection Reagents : 1% solutions of nitrates, chlorides or sulphates of cations were prepared in demineralized water.

Ammonium sulphide for Pb^{2+}, Ag^{+}, Tl^{+} and Bi^{3+}; potassium ferrocyanide for Fe^{3+}, Cu^{2+} and Uo_2^{2+}; dithizone in carbon tetrachloride for Cd^{2+} and Zn^{2+} and alcoholic dimethylglyoxime for Ni^{2+} and Co^{2+} were used as detection reagents.

SYNTHESIS OF ION-EXCHANGER GEL

Zirconium (IV) tungstophosphate was prepared by mixing 0.1M solutions of zirconium oxychloride, sodium tungstate and orthophosphoric acid in different volume ratios. The optimum volume ratio for better gel formation was found to be 1:1:1. The pH of the resultant gel was maintained around 1 by adding concentrated HNO_3 with constant stirring. The gel thus obtained was kept for 24 hours at room temperature before use.

CHROMATOGRAPHY

Preparation of Thin Layer Plates

The ion- exchanger gel was mixed with silica gel G in different ratios such as 3:1, 1:1 and 1:3 to obtain a slurry. This slurry was coated on thin glass plates (15 X 3 cm) with the help of an applicator (Toshinwal) to give a layer of 0.25 mm thickness. The plates were air dried first and then kept at 100± 5°C for 1 h in an electrically controlled oven. The plates were cooled to room temperature in a closed chamber before use. The various stationary and mobile phases used are listed below:

STATIONARY PHASE

S_1 = Plain silica gel G.

S_2 = S_1 + Ion - exchanger gel (1:1) w/w

S_3 = S_1 + Ion - exchanger gel (1:3) and (3:1) w/w

S_4 = S_2 impregnated with 0.1 - 2 M TBP in acetone.

S_5 = S_2 impregnatd with 1M TBP in acetone.

S_6 = S_3 impregnated with 1M TBP in acetone.

MOBILE PHASE

M_1 = 0.1, 0.5, 1 and 2M TBP

M_2 = 0.1% Benzo - 15 - crown - 6 in methanol.

M_3 = 0.1% Dibenzo 18 crown - 6 in a mixture of 1,4-dioxane and formic acid in 1:1 ratio.

M_4 = Water - HCl - acetone (10:0:90, 10:90:0, 0:10:90, 0:90:10, 90:10:0, 90:0:10, 50:50:0, 50:0:50, 0:50:50, 40:30:30, 30:40:30, v/v/v).

M_5 = 1, 10 and 26.5M formic acid.

M_6 = Water - formic acid - acetone (0:10:90, 8:2:90,10:0:90, 2:8:90, v/v/v).

M_7 = 1M Sodium formate - 1M KI (1:4, 4:1, 3:2, 1:1, v/v).

M_8 = 1M Sodium formate - 1M formic acid (1:1).

PROCEDURE

The TLC plates coated with mixed layer material were first run in methanol to remove excess acid and then the plates were run in the desired concentration of TBP in acetone for impregnation. This process of running the plate in the impregnant is called as the indirect impregnation method. The acetone from the TBP impregnated plates was completely removed by drying plates at 50°C for 1h. The test solutions of metal ions (3-5 μl) were spotted on to the TLC plates (S_1-S_6) with the help of a micropipette. The spots were dried at room temperature before development. The plates were developed in the chosen mobile phase by the ascending technique with a solvent run upto 10 cm in all cases. After development, the plates were air dried and the cations were detected by spraying the plates with appropriate chromogenic reagents. The values of R_L (R_F of the leading front) and R_T (R_F of the trailing front) were determined for each spot from which the R_F values of the cations were calculated.

$$R_F = 0.5(R_L + R_T)$$

5.3b RESULTS AND DISCUSSION

Zirconium tungstophosphate gel mixed with silica gel G was used as the layer material. The organophosphorous compound, tri-n-butylphosphate (TBP) was used in the concentration range 0.1- 2 M in acetone both as an eluent (i.e. mobile phase) and as an impregnant. TBP when used as impregnant in reversed - phase TLC (RPTLC), it yields better separations of metal ions compared to its use as mobile phase in normal - phase TLC. The optium impregnation concentration level was 1 M of TBP. The effect of formic acid concentation (1-10M) on the mobility of metal ions on S_1, S_2, S_4 and S_5 stationary phases was examined. Better results in terms of clear detection and compactness of spots of metal ions were obtained with 1.0 M formic acid eluent and

S_5 as stationary phase. Comparative studies of the mobility of metal ions in one of the selected mobile phases (mobile phase M_8) revealed that the R_F values of almost all metal ions except Pb^{2+} and Ag^+ on S_1 stationary phase were 1.0 while on S_2 stationary phase the R_F values of several metal ions were in the range 0.50 - 0.80. However, on stationary phases S_4 and S_5, the variation in R_F values of metal ions results in some important binary separations which are listed in Table 5.3.

Crown ethers were also tried as impregnants and as mobile phases with S_1-S_6 stationary phases in order to explore their utility in TLC separation of metal ions. 0.1% Benzo-15-crown-6 in methanol and 0.1% dibenzo 18 crown-6 in a mixture of 1,4- dioxane and formic acid in 1:1 ratio were used. The crown ether impregnated layers prepared from the mixture of ion - exchanger gel and silica gel in 1:1 ratio by weight were developed with 1.0M sodium formate +1.0M KI (3:2) and the unimpregnated layers were developed with M_2 and M_3. Generally, Ni^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+} produce tailed spots with both crown ethers, irrespective of their use as impregnant or as mobile phase. However, less tailed spots were observed when benzo-15-crown-6 was used as impregnant compared to its use as mobile phase whereas less tailed spots were noticed when dibenzo 18 crown-6 was used as eluent compared to its use as impregnant. Besides these; aqueous - organic mixed solvent systems (water - HCl - acetone, water - formic acid - acetone) and sodium formate - KI (M_7) were also used as mobile phases mainly with S_1, S_2 and S_5 stationary phases. The separations achieved in these systems are given in Table 5.3.

Table 5.3 :Separation of Some Metal Ions Achieved Under Different Experimental Conditions.

Stationary Phase	Mobile Phase	Separations (R_F)
Ion-exchange gel + Silica gel G (1:1)	Water + HCl + Acetone (0 + 10 + 90)	Cu^{2+}(0.90) - Pb^{2+}(0), UO_2^{2+}(0.90) - Pb^{2+}(0), Cd^{2+}(0.80) - Pb^{2+}(0), Co^{2+}(0.70) - Pb^{2+}(0)
	Water + HCl + Acetone (8 + 2 + 90)	Co^{2+}(0.80) - Tl^{+}(0), Cd^{2+}(0.80) - Tl^{+}(0), Cu^{2+}(0.70) - Tl^{+}(0), UO_2^{2+}(0.70) - Tl^{+}(0)
	Water + HCl + Acetone (10 + 0 + 90)	Cd^{2+}(0.75) - Cu^{2+}(0), Cd^{2+}(0.75) - UO_2^{2+}(0.15) Cd^{2+}(0.75) - Pb^{2+}(0), Cd^{2+}(0.75) - Tl^{+}(0), Ni^{2+}(0.70) - Cu^{2+}(0), Ni^{2+}(0.70) - UO_2^{2+}(0.15) Ni^{2+}(0.70) - Pb^{2+}(0), Ni^{2+}(0.70) - Tl^{+}(0)
	Water + Formic Acid + Acetone (8 + 2 + 90)	Co^{2+}(0.10) - Cu^{2+}(0), Co^{2+}(1.0) - Ag^{+}(0.25), Co^{2+}(1.0) - Pb^{2+}(0), Co^{2+}(1.0) - Tl^{+}(0), Co^{2+}(1.0) - Bi^{3+}(0), Cd^{2+}(1.0) - Ag^{+}(0.25) Cd^{2+}(1.0) - Pb^{2+}(0), Cd^{2+}(1.0) - Tl^{+}(0), Cd^{2+}(1.0) - Bi^{3+}(0)

Stationary Phase	Mobile Phase	Separations (R_F)
	Water + Formic Acid + Acetone (2+8+90)	Cd^{2+}(1.0) - Co^{2+}(0.10), Cd^{2+}(1.0) - Cu^{2+}(0), Cd^{2+}(1.0) - UO_2^{2+}(0), Cd^{2+}(1.0) - Ag^{2+}(0.20) Cd^{2+}(1.0) - Pb^{2+}(0), Cd^{2+}(1.0)-Tl^{+}(0), Cd^{2+}(1.0)-Bi^{3+}(0)
Ion-exchange gel +silica gel G (1:1) impregnation by 1M TBP in acetone	Distilled water	Ni^{2+}(0.76) - Pb^{2+}(0), Ni^{2+}(0.76) - Bi^{3+}(0), Ni^{2+}(0.76) - Tl^{+}(0.14), Ni^{2+}(0.76) - UO_2^{2+}(0.10) Ni^{2+}(0.76) - Fe^{3+}(0.10)
	1M Formic Acid	Cu^{2+}(0.80) - Pb^{2+}(0) Cu^{2+}(0.80) - Tl^{+}(0.0), UO_2^{2+}(0.80) - Pb^{2+}(0), UO_2^{2+}(0.80) -Tl^{+}(0.10)
	10M Formic Acid	Co^{2+}(0.80) - Pb^{2+}(0), Co^{2+}(0.80) - Ag^{+}(0.15), Cd^{2+}(0.75) - Pb^{2+}(0), Cd^{2+}(0.75) - Ag^{+}(0.15),
	Pure Formic Acid	Tl^{+}(0.65) - Pb^{2+}(0)
	Water + HCl + Acetone (8 + 2 + 90)	Cu^{2+}(1.0) - Pb^{2+}(0), Cu^{2+}(1.0) - Tl^{+}(0), Cu^{2+}(1.0) - Ag^{+}(0.15), UO_2^{2+}(1.0) - Pb^{2+}(0), UO_2^{2+}(1.0) - Tl^{+}(0), UO_2^{2+}(1.0) - Ag^{+}(0.15), Cd^{2+}(1.0) - Pb^{2+}(0), Cd^{2+}(1.0) - Tl^{+}(0), Cd^{2+}(1.0)- Ag^{+}(0.15), Co^{2+}(0.80) - Pb^{2+}(0), Co^{2+}(0.80) - Tl^{+}(0), Co^{2+}(0.80) - Ag^{+}(0.15)

Stationary Phase	Mobile Phase	Separations (R_F)
	Water + HCl + Acetone (0 + 10 + 90)	UO_2^{2+}(0.70) - Pb^{2+}(0), UO_2^{2+}(0.70) - Tl^{+}(0)
	Water + HCl + Acetone (2 + 8 + 90)	UO_2^{2+}(0.90) - Tl^{+}(0), Cd^{2+}(0.90) - Tl^{+}(0), Cu^{2+}(0.80) - Tl^{+}(0), Ni^{2+}(0.80) - Tl^{+}(0), Co^{2+}(0.75) - Tl^{+}(0)
	Water+Formic Acid+Acetone (2 + 8 + 90)	UO_2^{2+}(0.80) - Pb^{2+}(0), UO_2^{2+}(0.80) - Tl^{+}(0), UO_2^{2+}(0.80) - Ag^{+}(0.10), Co^{2+}(0.65) - Pb^{2+}(0), Co^{2+}(0.65) - Tl^{+}(0), Co^{2+}(0.65) - Ag^{+}(0.10)
	Water+Formic Acid+Acetone (10 + 0 + 90)	UO_2^{2+}(0.52) - Pb^{2+}(0), UO_2^{2+}(0.52) - Tl^{+}(0.05) UO_2^{2+}(0.52) - Ag^{+}(0.10), UO_2^{2+}(0.52) - Cu^{2+}(0), UO_2^{2+}(0.52) - Ni^{2+}(0.15)
	Water+Formic Acid+Acetone (8 + 2 + 90)	UO_2^{2+}(0.50) - Pb^{2+}(0), UO_2^{2+}(0.5) - Cu^{2+}(0.10), UO_2^{2+}(0.50 - Co^{2+}(0.15), Cd^{2+}(0.50) - Pb^{2+}(0), Cd^{2+}(0.50) - Cu^{2+}(0.10), Cd^{2+}(0.50) - Co^{2+}(0.15)
	Water+Formic Acid+Acetone (0 + 10 + 90)	UO_2^{2+}(0.55) - Pb^{2+}(0), UO_2^{2+}(0.55) - Tl^{+}(0), UO_2^{2+}(0.55) - Ag^{+}(0.08), UO_2^{2+}(0.55) - Cu^{2+}(0), UO_2^{2+}(0.55) - Ni^{2+}(0.15), UO_2^{2+}(0.55) - Co^{2+}(0), UO_2^{2+}(0.55) - Fe^{3+}(0.15)

Stationary Phase	Mobile Phase	Separations (R_F)
	Water + HCl + Acetone (90 + 10 + 0)	Cd^{2+}(0.80) - Ag^{+}(0), Cd^{2+}(0.80) - Pb^{2+}(0), Cd^{2+}(0.80) - Fe^{3+}(0)
	Water + HCl + Acetone (90 + 0 + 10)	Cu^{2+}(0.80) - Pb^{2+}(0), Cu^{2+}(0.80) - Tl^{+}(0.15), Cu^{2+}(0.80) - Bi^{3+}(0), Cd^{2+}(0.80) - Pb^{2+}(0), Cd^{2+}(0.80) - Tl^{+}(0.15), Cd^{2+}(0.80) - Bi^{3+}(0), Ni^{2+}(0.76) - Pb^{2+}(0), Ni^{2+}(0.76) - Tl^{+}(0.15), Ni^{2+}(0.76) - Bi^{3+}(0)
	Water + HCl + Acetone (50 + 50 + 0)	Ni^{2+}(0.80) - Fe^{3+}(0), Ni^{2+}(0.80) - Ag^{+}(0)
	1M Sod. Formate-1M Formic Acid (1:1)	Zn^{2+}(0.90) - Pb^{2+}(0), Zn^{2+}(0.90) - Tl^{+}(0), Zn^{2+}(0.90) - Bi^{3+}(0.10), Zn^{2+}(0.90) - Co^{2+}(0.15)
	1M Sod. Formate + 1M KI (20 : 80)	Co^{2+}(0.70) - Cu^{2+}(0), Co^{2+}(0.70) - Cd^{2+}(0), Co^{2+}(0.70) - Zn^{2+}(0.2), Co^{2+}(0.70) - Tl^{+}(0), Co^{2+}(0.70) - Bi^{3+}(0.05)
	1M Sod. Formate - 1M KI (80 : 20)	Co^{2+}(0.65) - Cu^{2+}(0.10, Co^{2+}(0 65) - Cd^{2+}(0), Co^{2+}(0.65) - Tl^{+}(0), Co^{2+}(0.65) - Bi^{3+}(0),

Stationary Phase	Mobile Phase	Separations (R_F)
		Ni^{2+}(0.65) - Cu^{2+}(0.10), Ni^{2+}(0.65) - Cd^{2+}(0), Ni^{2+}(0.65) - Tl^{+}(0), Ni^{2+}(0.65) - Bi^{3+}(0)
	1M Sod. Formate - 1M KI (60 : 40)	Ni^{2+}(0.85) - Cu^{2+}(0), Ni^{2+}(0.85) - Cd^{2+}(0) Ni^{2+}(0.85) - Ag^{+}(0), Ni^{2+}(0.85) - Pb^{2+}(0), Ni^{2+}(0.85) - Tl^{+}(0), Ni^{2+}(0.85) - Bi^{3+}(0), Co^{2+}(0.65) - Cu^{2+}(0), Co^{2+}(0.65) - Cd^{2+}(0), Co^{2+}(0.65 - Ag^{+}(0), Co^{2+}(0.65) - Pb^{2+}(0), Co^{2+}(0.65) - Tl^{+}(0), Co^{2+}(0.65) - Bi^{3+}(0)
Ion-exchanger gel + Silica gel G (3:1) impregnation by 1M TBP in acetone	1M sodium formate - 1M KI (20:80)	Ni^{2+}(0.80) - Cu^{2+}(0.05), Ni^{2+}(0.80) - UO_2^{2+}(0), Ni^{2+}(0.80) - Zn^{2+}(0.17), Ni^{2+}(0.80) - Pb^{2+}(0), Ni^{2+}(0.80) - Tl^{+}(0), Ni^{2+}(0.80) - Bi^{3+}(0)
	1M Sod. Formate - 1M KI (80 : 20)	Ni^{2+}(0.75) - Cu^{2+}(0), Ni^{2+}(0.75) - Pb^{2+}(0), Ni^{2+}(0.75) - Tl^{+}(0), Ni^{2+}(0.75) - Bi^{3+}(0)
	1M Sod. Formate - 1M KI (60: 40)	Ni^{2+}(0.65) - Cd^{2+}(0), Ni^{2+}(0.65) - Pb^{2+}(0), Ni^{2+}(0.65) Tl^{+}(0), Ni^{2+}(0.75) - Bi^{3+}(0), Ni^{2+}(0.65) - Cu^{2+}(0.05)

Stationary Phase	Mobile Phase	Separations (R_F)
	1M Sod. Formate - 1M KI (50:50)	Fe^{3+}(0.65) - Cu^{2+}(0.05), Fe^{3+}(0.65) - Cd^{2+}(0.10), Fe^{3+}(0.65) - Pb^{2+}(0), Fe^{3+}(0.65) Tl^{+}(0), Fe^{3+}(0.65) - Bi^{3+}(0)
Ion-exchange gel +Silica gel G (1:3) impregnation 1M TBP in acetone	1M Sod. Formate - 1M KI (80: 20)	Ni^{2+}(0.72) - Fe^{3+}(0.05), Ni^{2+}(0.72) - Cu^{2+}(0.10) Ni^{2+}(0.72) - Pb^{2+}(0), Ni^{2+}(0.72) - Tl^{+}(0), Ni^{2+}(0.72) - Bi^{3+}(0).

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CHAPTER VI

SEPARATION OF AROMATIC AMINES WITH WATER-IN-OIL MICROEMULSION SYSTEM

6.1 INTRODUCTION

Microemulsions are thermodynamically stable microstructured mixtures containing oil (nonpolar solvent), water, surfactant and often an amphiphilic molecule, called as cosurfactant (1). Unlike ordinary macroemulsions, however, microemulsions appear to be absolutely stable towards phase separation (2). The microemulsion systems are optically clear because of their much smaller droplet size (0.01-0.1mm) compared to the droplet size of macroemulsions (0.4-10mm). A microemulsion is formed when a cosurfactant (medium short chain alcohols or amines) is added to coarse-emulsion, water-surfactant oil (3-5) upto clarity. These microemulsions are also called swollen micellar solutions due to having similar structures as of micellar solutions with a difference that they have a core either of water or of hydrophobic fluids (normally hydrocarbons). Microemulsions are generally found in two forms (a) an oil-in-water microemulsion (o/w type) and (b) a water-in-oil (w/o type). In the former case, oil microdroplets enclosed in surfactant - cosurfactant film are dispersed in the continuous water phase whereas in the latter case water phase is dispersed as globules in the continuous oil phase.

Micellar systems have been extensively studied by physical chemists and biochemists for many years (6). However, it is only recently, that many analytical chemists have realized that micellar systems can often be advantageously applied to chemical analysis. These systems offer the unique capability of simultaneous separation of ionic and non-ionic compounds, solubilization of hydrophobic compounds in aqueous solutions, organization of reactants on a molecular level to increase the proximity of reagents and analytes and enhanced luminescence detection (7,8). One of the areas of great interest has been in the use of micellar systems as mobile phases in reversed - phase liquid chromatography (9-14) because of their unique separation selectivities. Though, micellar mobile phases provide a combination of remarkable advantages in chemical analysis that is not offered by any single high pressure liquid chromatographic (HPLC) method but the poor

chromatographic efficiency of micellar liquid chromatography has been the major disadvantage. This problem was solved by Dorsey et al. (15) for sodium dodecyl sulphate (SDS) surfactant by the addition of 3% 1- propanol to the micellar mobile phase which serves to wet the hydrophobic surface and speed up the mass transfer process across the phase boundary.

According to literature, most of the analytical applications of micellar solutions both normal (micelles formed in polar solvent) and reversed (surfactants dissolved in nonpolar solvents) micelles as mobile phases have been limited to HPLC and their use in thin layer chromatography (TLC) has largely been ignored. In fact a handbook of thin layer chromatography published in 1996 does not refer to use of any microemulsion system as mobile phase in it's chapter on TLC of phenols, aromatic carboxylic acids and indoles (16). Similarly, a review on planar chromatography by J. Sherma (17) published in 1994 did not report any work on the use of micelle or microemulsion as mobile phase in TLC analysis of amines. However, silica gel layers impregnated with 1% of the surfactant Triton - X100 has been utilized to separate some aromatic amines (18).

Bearing in mind the remarkable separation selectivity of micellar mobile phases that arises from a variety of environments, including a hydrophobic organic core and a polar charged surface which impart specific solubilization to hydrophobic, ionic and amphiphilic species, an extensive investigation has been initiated in our laboratory in order to find out superior chromatographic systems for rapid TLC analysis of aromatic amines. We used several cationic, anionic and non-ionic surfactants below, near and above their critical micelle concentration (CMC) in aqueous media as impregnant to sorbent phases (silica gel, alumina, kieselguhr, egg shell powder, kaolin etc.) as well as mobile phases to achieve better separations of metal ions, anions, metal chlorosulphates, amines and phenols by TLC but our hopes were belied.

However, efforts bore fruits when w/o microemulsion was utilized as novel eluent in TLC separation of anions (19). Here we report the application of water-in-oil microemulsion, consisting of SDS/n-pentanol/water/heptane, as mobile phase for the separation of aromatic amines from their mixtures on alumina thin layers.

6.2 EXPERIMENTAL

Apparatus : A TLC apparatus (Toshniwal, India) was used to prepare thin layers (0.25mm) of various adsorbents on 20x3 cm glass plates. Glass jars (29x6 cm) were used for the development of chromatographic plates.

Chemicals and Reagents : Specially pure sodium dodecyl sulphate (SDS) BDH, India; N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB), Romali, India; n-heptane (99%) CDH, India were used. n-pentanol (99%) was a Riedel product. Alumina, microcrystalline cellulose, kieselguhr, silica gel G, silica gel H were from CDH laboratories, India. All other chemicals were of analar grade.

Amines Studied : Aniline (AL), diphenylamine (DPA), p-nitroaniline (p-NAL), o-nitroaniline (o-NAL), o-chloroaniline (o-CAL), p-chloroaniline (p-CAL), N, N-dimethylaniline (DMAL), indole (ID), carbazole (CZ), m-nitroaniline (m-NAL), m- chloroaniline (m-CAL), p-dimethylaminobenzaldehyde (p-DAB) and p-dimethylaminocinnamaldehyde (p-DAC). All amines were procured from CDH, India and were of analytical reagent grade.

Test Solutions : The test solutions (1%) of all amines were prepared in methanol. Solutions of nitrates or chlorides of lead, silver, mercury, zinc, nickel and copper sulphate were prepared in demineralized water. Similarly 1% solutions of various anions were also prepared in demineralized water while that of phenols were prepared in methanol.

Detection : All amines were detected by exposing the TLC plates to iodine vapours except carbazole which showed fluorescence when exposed to UV radiation.

Chromatographic Systems : The various sorbents used as stationary phase are as follows :

S_1 - Microcrystalline cellulose

S_2 - Alumina

S_3 - Silica gel G

S_4 - Silica gel H

S_5 - Kieselguhr

Mobile Phases : The w/o microemulsion, used as mobile phase was prepared by titrating a coarse emulsion of n-heptane or n-hexane (160 ml), water (8 ml) and SDS or CTAB (8 g) with n-pentanol (25 ml). The microemulsion was produced at 30°C. The different mobile phases used were :-

M_1 - SDS-water-n-heptane-n-pentanol (8 g:8 ml:160 ml:25 ml)

M_2 - SDS-water-n-hexane-n-pentanol (8 g:8 ml:160 ml:25 ml)

M_3 - CTAB-water-n-heptane-n-pentanol (8 g:8ml:160 ml:25 ml)

M_4 - SDS - water-n-heptane-n-butanol (8 g:8 ml:160 ml:25 ml)

Preparation of TLC Plates : The TLC plates were prepared by mixing the sorbent with demineralized water in 1:3 ratio by weight with constant shaking to obtain a homogeneous slurry. The resultant slurry was applied to clean glass plates with the help of an applicator to give a 0.25 mm thick layer. The plates were dried at room temperature and then activated at 100±5°C by heating in an electrically controlled oven for 1 h. The activated plates were stored in closed chamber at room temperature until used.

PROCEDURE

0.05 ml of the test solution was spotted on a thin layer plate with the help of a micropipette about 2.0 cm above the lower edge of the TLC plate. The spots were allowed to air dry and the plates were developed in chosen mobile phase by one - dimensional ascending technique, in glass jars. The solvent ascent was fixed to 10 cm from the point of application in all cases. After development was complete the plates were removed from jars

and allowed to dry at room temperature. These TLC plates were then exposed to iodine vapors for about 10 min and then the spots were visualized under UV lamp except in case of carbazole where it is directly exposed to UV radiation without exposure to iodine vapors. Carbazole shows blue fluorescence in presence of UV light while most other amines show yellowish brown spot. The R_F values $R_F = (R_L+R_T)/2$ of these amines were determined by measuring R_L (R_F of leading front) and R_T (R_F of trailing front) values of the detected spots on TLC plate.

The limits of detection of various amines were determined by loading different amounts of amines on the chromatoplates, developing the plates and detecting the spots. The method was repeated with successive lowering of the amounts of amines until no spot was detected. The lowest amount of amine detected on the TLC plates was taken as the limit of detection.

To study the effect of the presence of metal ions, anions or phenols on the R_F value of amines and on the separations of DPA- p-NAL -p-CAL, a synthetic mixture of these impurities was prepared with amines in 1:1 ratio. The resultant mixture was spotted on chromatoplate and the spot was allowed to dry. The plates were developed, the spots were detected and the R_F values of the separated amines were determined from their R_L and R_T values.

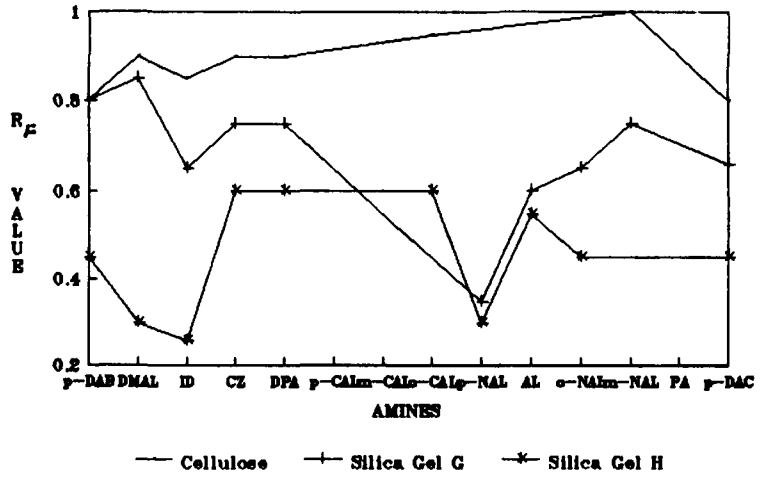
6.3 RESULTS AND DISCUSSION

The results obtained with aqueous micellar solutions of cationic (1% CTAB) and anionic (1% SDS) surfactants either as impregnants or as eluent could not produce desired separations of aromatic amines. Since the concentrations of the two surfactants used in aqueous solutions were higher than their respective CMCs (SDS 0.2% and CTAB 0.46%) it could be believed that the resultant test solutions were micellar solutions. The micellar systems could be considered as parental systems for complex systems like microemulsions, therefore, it was desirable to compare our w/o microemulsion system with ordinary SDS/CTAB micellar system. Although these two systems

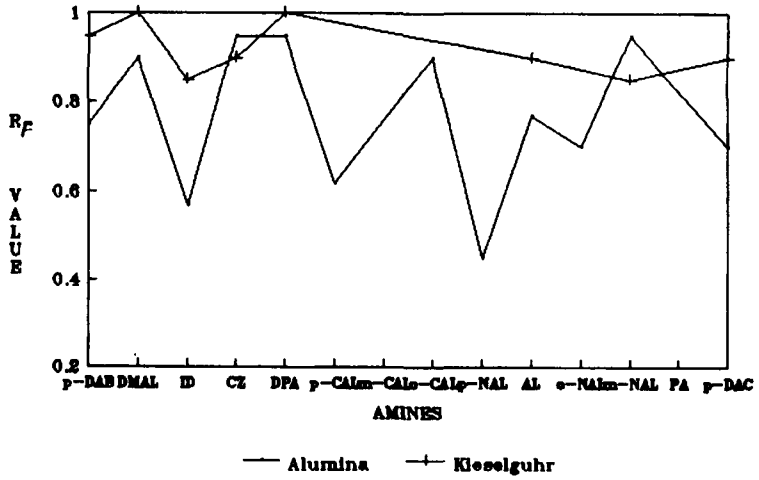
could not be considered similar due to different nature of the two associated assemblies. On switching over to microemulsion solutions from aqueous micellar solutions, some important separations were realized as a result of well formed compact spots of amines on TLC plates. Since it is difficult to prepare slurry of sorbents in microemulsion, we utilized the analytical potential of microemulsions using them as mobile phase with various stationary phases. The microemulsions (M_1 - M_4) prepared were transparent, clear and stable at room temperature (~30°C) for several weeks.

From the results depicted in Figs. 6.1(a) and (b) separation possibilities for amines are highest with alumina compared to other sorbent phases. Separation efficiency of various adsorbents follows the order: alumina > silica gel G = silica gel H > kieselguhr > cellulose. The amines producing compact spots (R_L - $R_T \leq 0.3$) only have been taken for plotting in Figures 6.1-6.3. These pronounced affinity differences of alumina towards aromatic amines is a happy consequence which provides interesting separation selectivities for amines. Thus, alumina and silica gel (both inorganic adsorbents) offer better separation possibilities compared to cellulose, an organic adsorbent. Kieselguhr, an inert adsorbent, with low surface activity has wider applications in partition chromatography and it's use in adsorption TLC is limited. In earlier investigations (19) kieselguhr has been found very useful for resolving anions but in the present study of amines it does not give satisfactory results.

In the present study, we selected alumina as stationary phase because of it's unique selectivity. The hydroxyl groups and oxide ions control the adsorption mechanism of amines. On the other hand, the w/o microemulsion exerts a preferentially solubilization effect on amines and thus modify their retention behaviour leading to improved separations.



1 (a)



1 (b)

Fig. 6.1 : (a) and (b) Separation Possibilities and Mobility of Amines on Different Sorbents.

In order to select a better surfactant for the preparation of w/o microemulsion, we substituted SDS by CTAB and the resultant microemulsion was used as mobile phase for studying the retention behaviour of amines on alumina layers. The results of this study are shown in Fig. 6.2 from where it can be safely concluded that CTAB yields poorer separation efficiency. The R_F values for most amines fall in the range 0.6 - 0.8 disclosing the fact that CTAB, a cationic surfactant is not suitable for achieving good separations of amines. Conversely, SDS (an anionic surfactant) yields excellent separations of amines on alumina layers. The microemulsions (M_1 and M_3) have identical composition of all components and both the surfactants have almost the same aggregation number (CTAB 61 and SDS 62) in aqueous solution at 25°C (20). It may, therefore, be inferred from Fig. 6.2 that the nature of polar charged surface of micellar systems imparts a detrimental effect on the retention behaviour of solute during migration through a polar adsorbent. CTAB microemulsion (M_3) on mixing with SDS microemulsion (M_1) results in the formation of precipitate and hence their mixtures could not be used as mobile phase. Similarly, mixtures of aqueous salt solutions (1.0M sodium chloride or ammonium sulphate) and microemulsion also resulted in the formation of a precipitate and could not be used as mobile phase. Instead, when microemulsion was saturated with powdered ammonium sulphate or sodium chloride salt and used as mobile phase, no change in mobility of amines was noticed. However, the spots got smeared. Earlier reports (21, 22) indicate that the addition of small concentration of salt into the micellar solution increases the micellar size and oil solubility. Thus, in present case it appears that the effect of salt concentrations in extracting water from the homogeneous phase and making the microemulsion droplets more compact fails to change the retention behaviour of amines on alumina layers. In view of the above facts, a chromatographic system alumina and SDS-water-heptane-pentanol microemulsion as mobile phase was selected for detailed study.

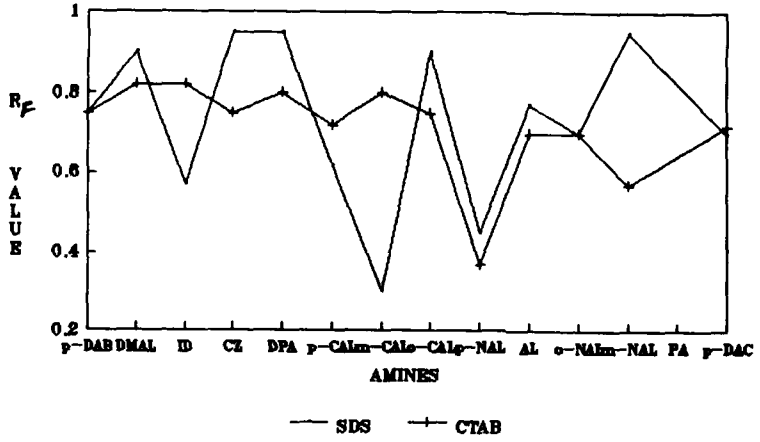


Fig. 6.2: Retention Pattern of Amines on Alumina Thin Layers in SDS (M_3) and CTAB (M_3) Microemulsions

(ΔR_F = R_F in S_2M_2 – R_F in S_1M_1)

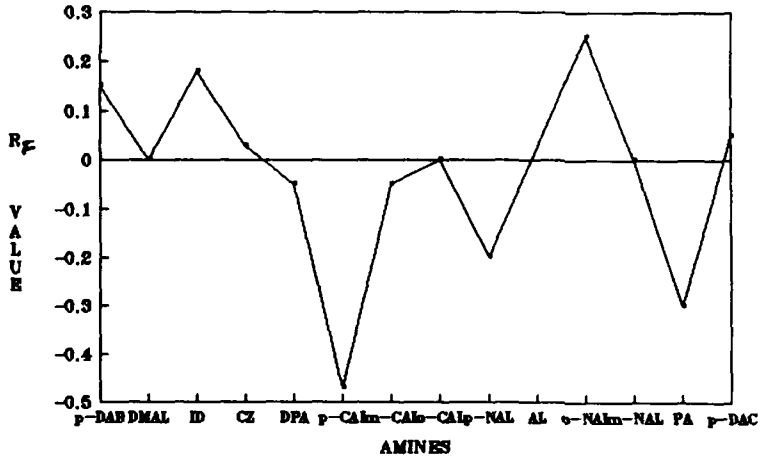


Fig. 6.3: Variation in Mobility of Amine on Alumina When Heptane (M_1) is Replaced by Hexane (M_2) in Microemulsion

The examination of mobility of amines on alumina by replacing heptane in M_1 with hexane (mobile phase M_2) reveals that the retention pattern of amines on alumina is changed which provides some new separations e.g. p-CAL from o-CAL and p-DAB. The ΔR_F values (R_F on alumina with SDS-water-heptane-pentanol — R_F on alumina with SDS-water-hexane-pentanol) of amines have been plotted in Fig. 6.3. The positive ΔR_F values for p-DAB, indole, o-NAL are indicative of higher mobility in hexane system (M_2). Conversely, p-CAL and p-NAL move faster in heptane system (M_1). All other amines show identical mobility ($\Delta R_F \sim 0$) in both the systems (M_1 and M_2). No microemulsion was produced when heptane or hexane was replaced by benzene, a closed-chain hydrocarbon. Instead of a clear microemulsion solution, a turbid system is formed when pentanol is added to mixture of water, surfactant and benzene. Figure 6.4 shows the retention behaviour of amines corresponding to the position of their substituent groups in the phenyl group. The higher mobility of the ortho isomer compared with the para isomer in both CAL and NAL may be attributed to the predominant steric effect of groups substituted at the ortho position. The much lower R_F value of m-CAL in comparison to m-NAL may be explained on the basis of strongly deactivating characteristics of m-directing nitro group compared to the o- and p-directing chlorine which offers mild deactivating effect on benzene ring. (27).

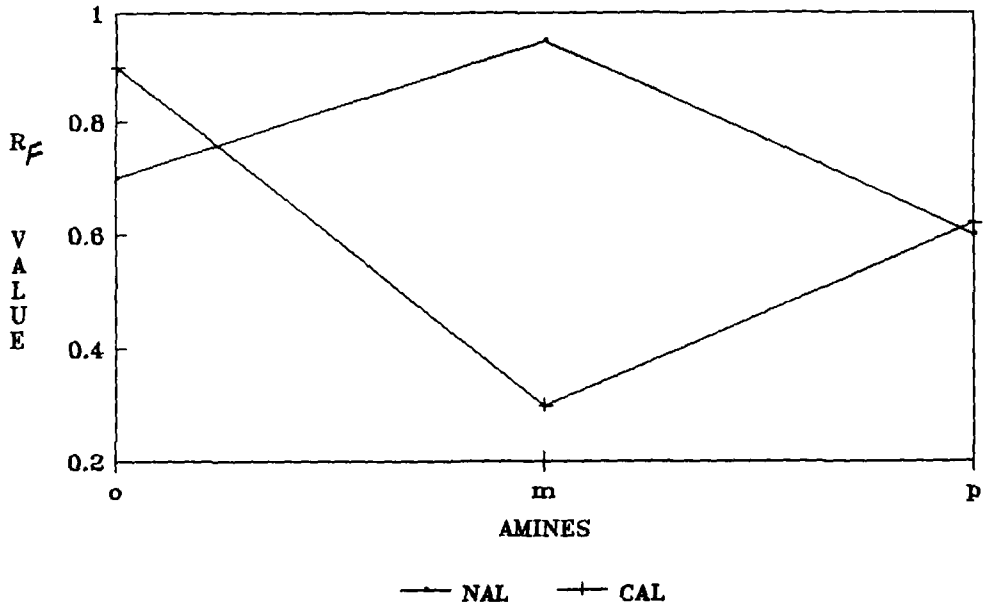


Fig. 6.4:Mobility Sequence of Chloro and Nitro Anialine Isomers in S_2– M_1 System

Table 6.1 summarizes some separations of amines by using some w/o microemulsions as mobile phase and alumina and cellulose as the stationary phase, separations achieved were well resolved and compact in this chromatographic system. The detection and dilution limits of amines are recorded in Table 6.2. The proposed method is highly sensitive for diphenylamine and indole, which can be detected easily to the extent of 0.04μg. The higher sensitivity (or lower detection limit) achieved by the proposed technique compared to earlier method (detection limit of DPA, 5×10^{-1} μg) (23) may be attributed to the localization of an amine in the hydrophobic core of w/o microemulsion.

Table 6.1 : Separations Achieved Experimentally on Alumina and Cellulose Layers Developed with Microemulsion Systems Containing SDS, Pentanol and Heptane or Hexane.

Stationary Phase	Mobile Phase	Separations (R_F values)
Microcrystalline cellulose	M_1	p-CAL (0) - ID (0.20)
Alumina	M_1	DPA (0.82) - p-CAL (0.60) - p-NAL (0.20)
		ID (0.60) - CZ (0.85)
		ID (0.60) - DPA (0.78)
		p-NAL (0.43) - m-NAL (0.61)
	M_2	p-CAL (0.69) - DPA (0.83)
		p-CAL (0.50) - 0-CAL (0.83)
		p-CAL (0.80) - p-DAB (0.65)
	M_3	p-NAL (0.33) - DMAL (0.63)
		p-NAL (0.39) - ID (0.67)
		m-NAL (0.35) - DPA (0.65)

Table 6.2 : Detection and Dilution Limits of Amines on Alumina Layers Developed with M_1

Amines	Lower limit of detection (μg)	Dilution* limit
Diphenylamine	$4x10^{-2}$	1:250,000
p-Nitroaniline	$2x10^{-1}$	1:50,000
Indole	$4x10^{-2}$	1:250,000
Carbazole	$2x10^{-1}$	1:50,000
p-Chloroaniline	$2x10^{-1}$	1:50,000

*Dilution limit = 1: (volume of test solution $\times 10^6$)/[limit of detection (μg)]

Table 6.3 summarizes the effect of various additives on the DPA-p-CAL-p-NAL separation. Heavy metals by and large do not influence the separation, though the R_F values of amines are slightly changed from their standard values of 0.82, 0.62 and 0.20 for DPA, p-CAL and p-NAL respectively, due to the presence of heavy metals in the mixture. The presence of acetate and oxalate anions do not have deleterious effect on the separation but thiocyanate hampers the separation of DPA and p-CAL due to the elongation of their spots. However, p-NAL can be separated from DPA and p-CAL. The presence of phenols in the mixture of amines result into the formation of crescent shaped figures of detected spots of DPA. p-CAL could not be detected in the presence of resorcinol, 0-cresol and hydro-quinone and hence the separation is hampered.

Table 6.3 : Effect of Additives on Separation of a Three Component Mixture Consisting of DPA, p-CAL and p-NAL in 1:1:1 Ratio on Alumina Layer Developed with SDS-Water-Heptane-Pentanol System

Additives	Separation (R_F values)		
	DPA	p-CAL	p-NAL
1. Heavy metals			
a) Copper	(0.68)	(0.56)	(0.20)
b) Zinc	(0.67)	(0.56)	(0.18)
c) Nickel	(0.76)	(0.56)	(0.20)
d) Lead	(0.71)	(0.58)	(0.27)
e) Mercury	(0.71)	(0.60)	(0.18)
f) Silver	(0.72)	(0.57)	(0.20)
2. Anions			
a) Acetate	(0.78)	(0.65)	(0.17)
b) Oxalate	(0.83)	(0.65)	(0.17)
3. Phenols*			
a) Resorcinol	(0.85)	-	(0.22)
b) 0-Cresol	(1.0)	-	(0.20)
c) Aminophenol	(0.76)	(0.52)	(0.30)
d) Hydroquinone	(0.95)	-	(0.27)

* p-CAL could not be detected on TLC plate in the presence of resorcinol, o-cresol and hydroquinone.

From the data recorded in Table 6.4, it is evident that the mobility of almost all amines decreases with the decrease in the carbon-chain length of cosurfactant. The lower mobility (i.e. low R_F values) of amines in microemulsion containing butanol may be attributed to the higher water solubilization capacity of this microemulsion (M_4) compared to pentanol containing microemulsion (M_1). The water solubilization capacity of a microemulsion depends upon

the stability of the interface, which in turn depends upon the transfer of alcohol from the continuous oil phase to the interface. The transfer of alcohol from the continuous phase is also dependent on it's solubility in that phase. Compared to pentanol, butanol is partitioned more at the interface owing to its higher solubility in water. Thus, more butanol molecules are expected to be present at the interface in combination with the SDS molecules. This situation results in an enhanced degree of disorderness (24) at the oil-water interface, leading to the higher water solubilization capacity of a microemulsion compared to pentanol. Therefore, in butanol microemulsion the water pool is water plus butanol, resulting in a decrease of butanol concentration in oil phase and leading to a decrease, in the mobility of amines. It has been reported (25, 26) that the nature of cosurfactant together with the amount and nature of emulsifier have significant effect on the water solubilization capacity of a microemulsion system.

Table 6.4 : Mobility of Amines on Alumina Thin Layer With Pentanol (M_1) and Butanol (M_4) as Cosurfactant in the Microemulsion as the Mobile Phase.

Amines	M_1	M_4
p-DAB	0.75	0.67
DMAL	0.90	0.70
ID	0.57	0.45 T
CZ	0.95	ND
DPA	0.95	0.74
p-CAL	0.62	0.50
0-CAL	0.30 T	0
m-CAL	0.90	0.65
AL	0.95	ND
p-NAL	0.60 T	0.20 T
0-NAL	0.70 T	0.54
m-NAL	0.95	0.44
p-DAC	0.85 T	0.65

*T - Tailed Spot, ND - Not detected

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CHAPTER VII

SEPARATION AND IDENTIFICATION OF AMINES AND PHENOLS ON CHICKEN EGG-SHELL LAYERS

7.1 INTRODUCTION

Thin layer chromotography (TLC) is probably the simplest and most economic chromatographic methods for the detection and separation of microgram quantities of both organic and inorganic compounds (1-3). To achieve improved chromatographic performance in terms of selectivity, resolution and reproducibility, thin layers with new stationary phases (e.g. polyamides, derivatized celluloses, α-chitin, chitosan, aminoplast, polyacrylonitrile, chemically modified and impregnated hydrous solids etc.) have been introduced (4-10). In the absence of an ideal sorbent, the need of an inexpensive, reproducible and readily available stable sorbent phase for TLC has always been felt. The environment conciousness has renewed the interest for searching environmental friendly chromatographic systems. As a result some natural products, including biopolymers, have been examined to determine their suitability as stationary phases in chromatography (4). According to literature, the majority of TLC work on amines and phenols has been performed on silica layers, followed by chemically bonded reversed-phase layers, layers impregnated with complexing reagents, alumina, cellulose and ion-exchangers. Several TLC systems have been developed in recent past to obtain selective separations of amines and phenols using plain, impregnated, mixed and reversed-phase layers in combination with organic and organic-aqueous mobile phases (11-16). Studies on egg-shell powder as stationary phase for analysis of metal chlorosulphates (17) shows that egg-shell powder has tremendous potentiality in separation science.

Egg-shell is available in abundance all over the world and being white it has manifold possibilities for being used as low cost adsorbent. The present study is aimed to obtain the optimum conditions for developing an inexpensive TLC system using egg-shell powder as stationary phase for identification and separation of organic pollutants e.g.

amines and phenols. Heavy metal ions have been identified on TLC plates after separation from amines and phenols. The present investigation is useful to remove metallic impurities from organic substances and vice versa. Though very efficient gas and liquid chromotographic methods are available for the purification and separation of amines, a simple, rapid and inexpensive TLC method is still desirable and the proposed method fills this gap.

7.2 EXPERIMENTAL

Apparatus : TLC applicator (Toshniwal, India); 7.5×2.5cm glass plates and 10×4cm glass jars were used for the preparation and development of chromatographic plates.

Chemicals and Reagents : Acetone, cyclohexane, dimethylformamide (DMF), ethylacetate, ethylmethyl ketone (EMK), hexane, isobutylmethylketone (IBMK), toluene, tributylphosphate (TBP), tributyl amine (TBA), alumina, microcrystalline cellulose and silica gel H were obtained from Central Drug House, India. Butanol and dimethyl sulphoxide (DMSO) from Sarabhai M. Chemicals and pentanol from Reidel, Germany were used. Other chemicals and reagents were also of analytical grade. Chicken egg-shells were collected from natural source.

Amines and Phenols Studied : Aniline (AL), diphenylamine (DPA), p-nitroaniline (p-NAL), o-nitroaniline (o-NAL), o-chloroaniline (o-CAL), p-chloroaniline (p-CAL), N, N-dimethylaniline (DMAL), indole (ID), carbazole (CZ), m-nitroaniline (m-NAL), m-chloroaniline (m-CAL), p-dimethylaminobenzaldehyde (p-DAB), and p-dimethylaminocinnamaldehyde (p-DAC) were the amines studied. The phenolic derivatives were p-aminophenol (p-APh), m-cresol (m-Crol), gallic acid (GA), hydroquinone (Hqn), 2-naphthol (2-Nol), 2-nitrophenol (2-NPhl), p-nitrophenol (p-NPhl), orcinol (Ool), phloroglucinol (Phglol), picric acid (PA), pyro-

gallol (Pol), resorcinol (Rol) and thymol crystal (Tol).

Test Solutions : The test solutions 1% of all amines and phenols were prepared in methanol.

Detection : The detection of analytes were carried out by exposing the TLC plates to iodine vapours except for carbazole, which was visualized as blue fluorescent spot under UV radiation.

CHROMATOGRAPHIC SYSTEMS

Stationary Phases

No.	Composition
S_1	Calcium carbonate
S_2	Chicken egg-shell powder
S_3	Chicken egg-shell powder impregnated with 1% aq. $CuSO_4$
S_4	Chicken egg-shell powder impregnated with 10% aq. $CuSO_4$
S_5	Chicken egg-shell powder impregnated with 20% aq. $CuSO_4$
S_6	Chicken egg-shell powder impregnated with 0.2M TBA
S_7	Chicken egg-shell powder impregnated with 1M TBA
S_8	Chicken egg-shell powder impregnated with 0.2M TBP

Mobile Phases

	No.	Composition
(a) Organic Solvents		
	M_1	Acetone (5.4)[a)]
	M_2	n-butanol (3.9)
	M_3	Cyclohexane (0.0)
	M_4	Dimethylformamide (6.4)
	M_5	Dimethylsulphoxide (6.5)
	M_6	1,4 dioxane (4.8)
	M_7	Ethanol (5.2)

M_8	Ethylacetate (4.3)
M_9	Ethylmethylketone (4.8)
M_{10}	Hexane (0.00)
M_{11}	Isobutylmethyl ketone
M_{12}	Methanol (6.6)
M_{13}	Pentanol
M_{14}	Propanol
M_{15}	Tributylphosphate
M_{16}	Toluene (2.3)
M_{17}	1,4 dioxane-hexane [1:1 and 1:4]
M_{18}	Ethylacetate - hexane [1:4]

(b) Aqueous salt solutions

M_{19}	Aq. ammonium sulphate 0.001,0.05,0.10,1M
M_{20}	Aq. potassium thiocynate 1M.

a) Values in brackets refer to the polarity index.

Preparation of Chicken Egg-Shell Powder

Broken chicken egg shell pieces were washed with boiling water followed by washing with distilled water and soaked in 10% NaOH solution for a period of 20-30h to remove protien contents. The solution was drained off and the clean egg shell pieces were washed several times with distilled water to ensure complete removal of NaOH, dried at 100°C, ground and sieved to get the powder of 150-250 mesh size. The resultant egg shell powder was used to make the slurry for coating on TLC plates without addition of any binder.

Preparation of TLC Plates

The TLC plates were prepared by mixing the sorbent with demineralized water in 1:3 ratio by weight with constant shaking to obtain

a homogeneous slurry. The resultant slurry was applied to clean glass plates with the help of an applicator to give 0.25 mm thick layer. The plates were dried at room temperature and then activated at 100±2°C by heating in an electrically controlled oven for about 1h. The activated plates were stored in closed chamber at room temperature until used.

For impregnated plates the slurry was prepared by thorough mixing with the alcoholic solutions of TBP (1M), TBA (0.2M, 1M) or aqueous $CuSO_4$ (1,10 and 20%) for 5 minutes. Coating of plates was performed as for unimpregnated plates. No addition of any binder is required for the preparation of plates.

PROCEDURE

0.05 mL of the test solution was applied on TLC plates with the help of a micropipette at about 1.5 cm above the lower edge. The spots were air dried and the plates were developed with suitable mobile phase by ascending technique, in glass jars. The solvent ascent was fixed to 5 cm from the point of application in all cases. After development, the plates were taken out from the jars and subjected for drying at room temperature. The dried plates were then exposed to iodine vapours for about 10 min and then the spots were visualized under UV lamp, except in case of carbazole, where it was directly exposed to UV radiations without exposure to iodine vapors. Carbazole shows blue fluorescence under UV light while most other amines show yellowish brown spots.

7.3 RESULTS AND DISCUSSION

Investigations to develop new sorbent phases using novel materials resulted in the possible use of chicken egg-shell powder as an effective sorbent layer for the separation of inorganic complexes of some transition metals and rare earths (17). The results obtained were promising in spite of certain limitations of egg shell powder as it was unstable in acidic mobile phases.

Results of the present study have been summarized in Tables 7.1–7.3 and Fig. 7.1. Table 7.1 provides information about the mobility of phenols and amines in various chromatographic systems. Based on these data, certain conclusions have been made to obtain selective separation of phenols and amines and/or amines from phenols. A slight increase in the R_F values of amines was noticed with increase in molecular weight of alcohols or ketones in the mobile phase. However, this trend was not arbitrary, many amines and phenols showed decrease in R_F with increase in molecular weight of alcohols and ketones. AL, p-CAL, 2-CAL, 2-Nol, Tol and m-Crol were not detected at all in many alcohol or ketone systems. Picric acid gave tailed spots in most of the cases. Compared to alcohols, ketone systems gave more compact spots. The increased tailing of spots in alcohol systems was possibly due to the effect of intermolecular hydrogen bonding between solute (amines and phenols) and solvents.

Table 7.1 : hR_F (R_F ×100) Values of Phenols and Amines on Pure Egg-Shell Layers

	AMINES												PHENOLS												
Mobile phase[a)]	DMAL	ID	DPA	CZ	p-CAL	3-CAL	2-CAL	AL	m-NAL	o-NAL	p-NAL	p-DAC	p-NPhl	2-NPhl	Pol	2-Nol	Rol	m-Crol	GA	Tol	Hqn	p-APh	Ool	Phglol	α-Nol	PA
Methanol	75	-	70T	75T	-	90	50T	50T	70T	-	90T	80T	80T	70T	40T	-	0	-	45T	-	-	-	90	0	85T	-
Ethanol	80T	-	85T	85T	-	80T	90	-	90	90	90	90	85T	0	25T	90	0	70	20T	-	90	0	90	90	85	50T
Propanol	80	90	-	-	90	90	-	-	90	90	80T	99	90	0	20T	70	0	-	20T	-	80	80	80	0	85	30T
Butanol	80	85T	80T	80T	90	90	-	-	90	90	90	-	50T	0	10	-	0	0	0	-	75	0	80T	0	80T	50T
Pentanol	90	90	-	-	90	90	-	-	80T	90	90	-	90	0	10	-	0	-	05	-	75	0	84	0	84	30T
Acetone	80T	90	80T	90	-	0	80T	-	99	99	50T	0	50T	50T	0	0	0	-	0	-	0	0T	-	0	99	50T
EMK	60T	-	80T	80T	-	90	99	-	75T	75T	80T	90	85	85	25T	-	0	-	20T	-	50T	50T	80	0	85	50T
IBMK	50T	99	50T	90	0	0	-	-	99	99	99	80T	85	90	20T	-	0	-	15	-	0	0	90	0	90	35T

a) The mobile phases are arranged in increasing order of carbon chain length.

The possible separations of amines and phenols in some selected chromatographic systems have been listed in Table 7.2. It is apparent from the data that indole can be selectively separated from carbazole and diphenylamine on egg shell layers using cyclohexane (M_3), hexane (M_{10}), toluene (M_{16}) and ethylacetate-hexane in 1:4 ratio (M_{18}). Indole, carbazole and diphenylamine have similar structural features and hence their separation from each other is analytically important.

Table 7.2 : Experimentally Achieved Separations of Amines and Phenols on Pure Chicken Egg-Shell Layer (S_2)

Mobile Phase	Samples	Separations (R_F)
	Amines	
M_3		ID (0) - CZ (0.60)
M_{10}		ID (0) - DPA (0.90)
		ID(0) - o-NAL (0.35) - DPA (0.90)
		p-CAL (0) - o-NAL (0.30) - DPA (0.85)
		m-CAL (0) - o-NAL (0.25) - DPA (0.75)
		o-CAL (0) - o-NAL (0.30) - DPA (0.90)
		p-NAL (0) - o-NAL (0.35) - DPA (0.80)
		p-DAC (0) - o-NAL (0.55) - DPA (0.99)
		o-NAL (0.30) - DPA (0.85)
M_{16}		ID (0) - DPA (0.98)
M_{18}		ID (0) - DPA (0.99)
	Phenols	
M_1		2-Nol (0) - α-Nol (0.90)
M_7		p-NPhl (0.90) - 2-NPhl (0)
M_{16}		m-Crol (0.90) - Rol (0)
		m-Crol (0.90) - GA (0)
M_{18}		Pol (0) - Hqn (0.55) - 2-Nol (0.95)
		GA (0) - Hqn (0.55) - 2 Nol (0.95)
M_{19} (1M)		Ool (0.90) - p-APh (0)

Although hexane was found most useful for resolving a mixture of amines resulting in ternary separations but it failed to induce differential migration of phenols. Ethylacetate-hexane (1:4) system was found suitable for the separation of both phenols and amines. Some important binary separations of phenols were achieved on egg shell layers developed with acetone (M_1), ethanol (M_7), 1M ammonium sulphate (M_{19}) and toluene (M_{16}). The use of variable concentrations of aqueous ammonium sulphate (0.01 - 1.0M) as mobile phase showed the absence of salting-out effect on the mobility of phenols and amines. We could not observe a trend of increase in R_F values of phenols and amines with the decrease in the ammonium sulphate concentration. Salting-out TLC using ammonium sulphate solutions in water has been successfullly applied (18-19) for the analysis of metal complexes where the R_F values of the same type of complexes were found to decrease with increasing hydrophobic part of the complex.

Table 7.3 presents some separations of amines from phenols on impregnated and unimpregnated layers. Ethylacetate-hexane (1:4) gave lower R_F for amines and higher R_F for phenols on plain egg shell layers leading to the separation of amines from phenols. Use of 1,4-dioxane in place of ethylacetate with hexane (1:4) in the mobile phase reversed the trend of mobility by giving higher R_F for amines ($R_F \geq 0.80$) and lower R_F for phenols ($R_F \geq 0.20$). Increase in concentration of 1,4 dioxane in the mobile phase from 25-50% resulted in an increase in separation efficiency of amines from picric acid. Normally, the R_F of both amines and phenols increases with increase in polarity of solvent system. For example, most of the amines and phenols show higher mobility with acetone, DMF, DMSO, ethylacetate and ethanol whereas they remain almost at the point of application with hexane and toluene.

Table 7.3 : Separation of Amines from Phenols with Different Chromatographic Systems

Chromotographic System	Separations	
	Amines	Phenols
S_2 - M_3	DMAL, ID, DPA, o-CAL m-CAL, p-CAL, p-DAC (R_F = 0)	m-Crol ($R_F \geq 0.95$)
S_2 - M_{11}	p-CAL, m-CAL (R_F=0)	2-Nol (R_F = 0.90)
S_2 - M_{16}	p-CAL, m-CAL, o-CAL p-DAC, AL, o-NAL, DMAL ID (R_F = 0)	2NPhl, m-Crol ($R_F \geq 0.90$)
S_2 - M_{17} (1:1)	DMAL, ID, DPA, p-NAL ($R_F \geq 0.90$)	PA ($R_F \leq 0.20$)
S_2 - M_{17} (1:4)	DMAL ($R_F \geq 0.85$)	PA (R_F = 0)
S_2 - M_{18} (1:4)	ID, p-CAL, m-CAL, o-CAL, p-DAC (R_F = 0)	Hqn, 2-Nol ($R_F \geq 0.85$)
S_3 - M_{10}	DMAL ($R_F \geq 0.80$)	p-NPhl, Pol, Rol, m-Crol, GA, Hqn, p-Aph, Ool, Phglol (R_F=0)
S_4 - M_{10}	ID, o-NAL, m-NAL, 2-CAL ($R_F \geq 0.90$)	Phglol, Ool, GA, Hqn, 2-Nol, p-NPhl, Pol, Rol (R_F = 0)
S_6 - M_8	DMAL, p-NAL, o-NAL, m-NAL ($R_F \geq 0.90$)	Pol, Rol, Phglol (R_F = 0)
S_7 - M_{10}	DPA, AL, p-DAC ($R_F \geq 0.90$)	PA, Pol, Rol, GA, Hqn,p-APlh, Phglol, α-Nol (R_F = 0)

Egg shell layers impregnated with 1M TBA (S_7), 1% $CuSO_4$ (S_3) and 10% $CuSO_4$ (S_4) were also found useful for the separation of amines

from phenols. With all impregnated layers studied phenols remained at the point of application ($R_F \leq 0.10$) and amines showed higher mobility ($R_F \geq 0.80$). TLC plates prepared from egg-shell powder impregnated with 20% $CuSO_4$ solution were blue in colour. Amines and phenols produced bright coloured spots on these plates just after loading. Thus, all phenols and some amines were self detected and did not require any detection reagent. However, the increased tailing of amines on these layers developed with hexane (development time 1 min for 5 cm ascent) hampered the possibility of their separation from phenols. However, amines can selectively be separated from phenols by increasing the development distance to 10 cm instance of 5 cm.

Keeping in mind that calcium carbonate is the major component of pure egg shell, an attempt was made to compare the results obtained on pure egg shell with these achieved on $CaCO_3$ layers using hexane which gives over all better results as mobile phase. The results are shown in Fig. 7.1. Most of the amines gave either tailed spots or were not detected clearly on $CaCO_3$ layers. However, on egg shell layers improved detection and compactness for almost all amines studied were observed. Similarly, all the phenols gave compact spots on egg shell layers developed with hexane. Conversely, on $CaCO_3$ layers, 2-NPhl and 2-Nol gave tailed spots while m-cresol and thymol not be detected. Thus, these comparative results show that egg-shell powder behaves differently than that of $CaCO_3$. The present study, establishes the utility of chicken egg shell powder in classical TLC as an efficient sorbent material for the selective separation of organic pollutants. Further investigations are needed to explore its utility as stationary phase in TLC/HPTLC.

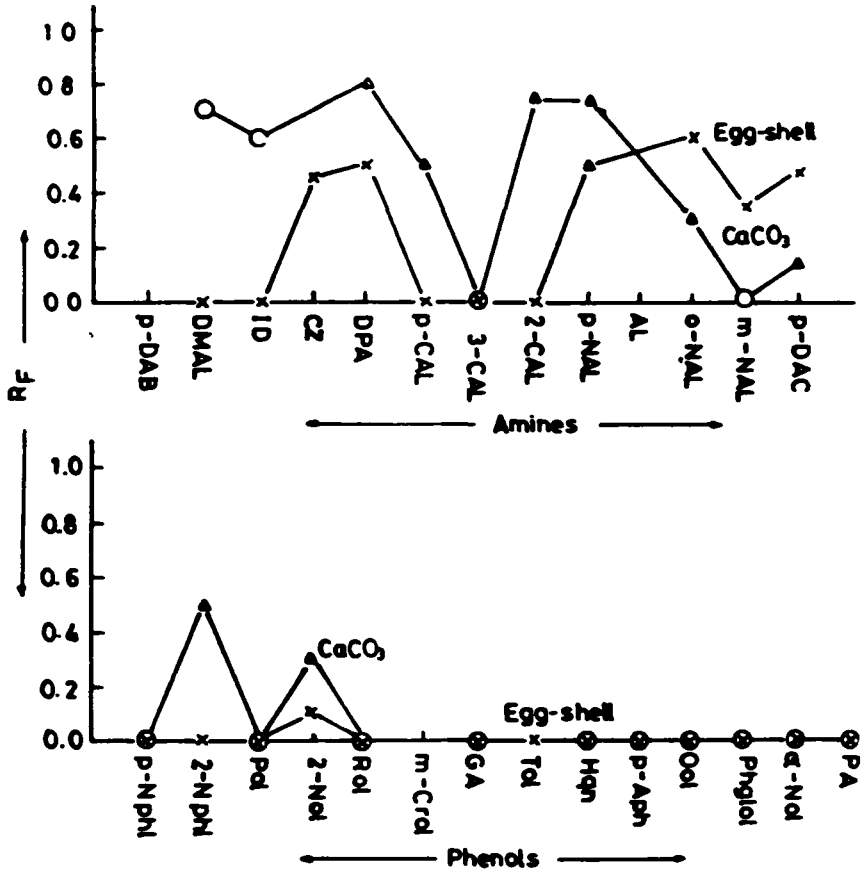

Figure 7.1: Mobility of amines and phenols on calcium carbonate and chicken egg-shell layers in hexane solvent system

△ Tailed spot RL - RT ≥ 0.30

⊗ Combined spots for egg-shell layers and $CaCO_3$ layers

○ Spots on $CaCO_3$ layers

× Spots on egg-shell layers

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Review

Twenty-Two Years Report on the Thin-Layer Chromatography of Inorganic Mixtures: Observations and Future Prospects

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Key Words

TLC
Inorganic species
Stationary phases
Mobile phases

Summary

This review encapsulates data published during 1973–1994 on the thin layer chromatography (TLC) of inorganic species. It presents the types of stationary phase, mobile phase, and technique involved in the separation, identification, and determination of inorganic substances present either singly or as components of closely related mixtures in a variety of matrices. Examples of the use of inorganic TLC or HPTLC for analysis of a wide range of synthetic and natural environmental, geological, biological, textile, and pharmaceutical samples are described. In most cases TLC in combination with other sophisticated analytical techniques is used for quantitative analysis. More application-oriented work with hyphenation of TLC or HPTLC and other developing techniques is expected in the near future.

1 Introduction

Despite the widespread use of TLC as a simple and low-cost analytical tool for the separation, identification, and semi-quantitative evaluation of organic, inorganic and organometallic species over the past 35 years, the technique is usually not considered to be highly efficient or quantitative. According to a recent survey [1] TLC has distinct advantages over HPLC, *e.g.* greater detection possibilities, more rapid throughput, use of disposable plates, easier sample preparation, low solvent consumption, and lower operating cost. The poorer separation efficiency and the influence of environmental conditions on the reproducibility of R_F values have, however, been major disadvantages of TLC compared with HPLC and GC. A major breakthrough in the field of TLC came in the early 1960s with the availability of convenient precoated plates [2]. It has recently been realized that modern high performance (HP) TLC rivals HPLC and GC in its ability to resolve complex mixtures and to provide analyte quantification. Other advantages of HPTLC over conventional TLC [3] include: improvements in the quality of sorbents and the consistency of plate manufacture; the use of optimized techniques and equipment for sample application, plate development, application of detection reagent, and densitometric scanning; and a greater understanding of chromatography theory.

Although the first published report [4] of TLC described the separation of inorganic species, the importance of inorganic TLC was not recognized until the beginning of the 1960s when *Seiler* [5–7] separated inorganic substances. *Meinhard* and *Hall* were among earlier investigators who separated inorganic ions around 1950 [8,9] by use of a mixture of aluminum oxide and celite as a layer on a microscope slide. Metal ions were, in fact, first separated in 1942 by paper chromatography in three different laboratories almost simultaneously [10–12].

Although several reviews, general and/or specific [13–37] and books and/or handbooks [38–43] have occasionally published literature on the TLC of inorganic substances, this area of research has not been included in the latest edition of the two-volume publication 'Chromatography' edited by *E. Heftmann* [43]. According to the literature, not a single review providing up-to-date data on inorganic TLC has appeared since the publication, in 1973, of a well documented review by *Brinkman et al.* which provided complete data on the TLC of inorganic and metal complexes published up to the end of 1972. The literature on inorganic TLC published after 1972 is scattered and usually found either in handbooks or review articles, some of which are

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pine copra. The last oral presentation of this session (**Prof Ian Wilson**) was concerned with the use of bonded phases (particularly C18 and DIOL) as a means of achieving separations that were difficult to obtain on silica.

In the afternoon the main poster session and exhibition of the meeting was held. Both the exhibition of TLC equipment and posters were in the same area, with the exhibitors stands around the outside of the room and posters in the middle ensuring that the delegates had easy access to both. The posters covered topics such as the use of TLC to determine the authenticity of vanilla extracts (**Salwa and Colin Poole**) HPTLC for natural products (**Skett and de Vine**) chemometrics (**Bazylak**), development chambers (**Dzido**) coal analysis (**Herold et al**), polycyclic aromatic hydrocarbons (**Moller and Sieber**) and the determination of drugs in plasma (**Taberner et al**) etc, basically almost the whole range of TLC techniques and applications was covered. Both exhibitors and poster presenters were kept busy answering questions, giving advice and providing explanations.

Contemporary TLC instrumentation, it may be the fastest quantification package ever, but will it make the tea as well?

The theme of giving and taking advice was continued in the separation clinic, where those of the delegates who had a particular problem with some aspect of planar techniques were encouraged to discuss them in an informal atmosphere. The separations clinic was an innovation for this meeting, and the organisers approached it with a certain amount of trepidation. However, in the opinion of several delegates the clinic was one of the most useful features of the symposium, and will certainly be seen in future TLC Forum meetings.

The final part of the scientific program for the day was the short presentations by the manufacturers on new products.

The last day of the meeting was devoted to the use of *in situ* spectroscopy for the identification of substances on TLC plates. HPTLC-MSMS and NMR were described by **Ian Wilson,** whilst the use of IR and Raman spectroscopy for TLC was covered by **David Crowther** (Sheffield Hallam University), with the meeting closed by **Colin Poole** who looked briefly into the future.

From the point of view of the organisers and delegates this was a very successful meeting that reinforced the spirit of the TLC Forum as a place to chance one knowledge of planar techniques and make friends. Although the Forum is essentially a UK-based organisation this meeting was greatly enhanced by the involvement of a number of quests and participants from the rest of Europe, and would not have been as much of a success without their participation. A special vote of thanks must also be given to the companies who supported the exhibition without which the registration fee would have been much higher for the delegates.

Three editors togather! Prof Nyiredy, Editor in-Chief of the JPC, Prof Poole, a former Editor of the JPC and presently an Editor of the Journal of Chromatography and Prof Wilson, another the Editor of the JPC sharing a few moments *between sessions at the conference.*

Hopefully many of the contributions to the meeting will eventually appear in print in the JPC. In the meantime anyone wishing to obtain a copy of the abstracts (or a particular abstract) should contact.

Ian Wilson

not easily accessible to many readers. Many review articles have appeared in languages (*e.g.* Chinese, German, Russian, Japanese) which are not as widely spoken as is English. The review is written with the aim of presenting a complete picture of work performed during 1973–94, inclusive, on TLC or HPTLC analysis of metal cations, anions, and complexes. The available information has been arranged in a very condensed form. No papers describing techniques, construction of apparatus, theory, and general aspects of TLC have been included, neither have reports of the use of TLC for the analysis of nonmetallic inorganic substances. It should be remarked that with the exception of a report by *Kovacs-Hadady* [44], who studied the interactions between alkali and alkaline earth metal ions on silica gel developed with aqueous solutions, overpressured layer chromatography (OPLC) has not been used for the analysis of inorganic mixtures, despite its having found several attractive applications in the analysis of organic compounds.

2 Results and Discussion

Literature published in the period 1973–1994 on the TLC analysis of metals and metal cations, of anions, and of metal complexes is presented in **Tables 1–3**, respectively; the tables give information about the various combinations of

Table 1

TLC of anions.[a)]

Anions	Stat. phase	Mobile phase	Comment	Ref.
Cl^-, ClO_4, Br, BrO_3, BrO_4, I, IO_3, IO_4, CNS, NO_2, ReO_4, CrO_4^{2-}, MoO_4^{2-}, $S_2O_3^{2-}$, SeO_3^{2-}, SeO_4^{2-}, TeO_3^{2-}, TeO_4^{2-}, AsO_3^{3-}, AsO_4^{3-}, PO_4^{3-}, VO_3^{4-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Cr_2O_7^{2-}$	S1	M1	Development time 30 min; qualitative separations	111
MoO_4^{2-}, TeO_4^{2-}, IO_3, RuO_4^{2-}, I	S2	M2	Ascending technique; run 10 cm; separation of molybdate, pertechnate, iodates, iodide, and ruthenate ions	112
S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, $S_2O_8^{2-}$, SO_4^{2-}, $S_2O_5^{2-}$	S3	M3	Qualitative separations; R_F values decreased in the order $SO_3^{2-} > S_2O_8^{2-} > S_2O_5^{2-}$	113
F^-, Cl^-, Br, I	S4	M4	Ascending technique; run 15 cm; layer thickness 0.25 mm	114
CN, SCN^-, NO_2, NO_3, Cl, Br, I ClO, ClO_3, ClO_4, IO_3, IO_4, BrO_3, CrO_4^{2-}, $Cr_2O_7^{2-}$, S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$, $H_2PO_4^-$, SeO_3^{2-}, TeO_3^{2-}	S14, S19	M5	Highly reproducible separations of anions	115
CN, SCN^-, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	S6	M6	Qualitative analysis of pseudohalides on silica gel	116
$Fe(CN)_6^{4-}$, MoO_4^{2-}, $S_2O_3^{2-}$, SO_3^{2-} CrO_4^{2-}, ReO_4^-, ClO_3^-, Cl, Br^-, I, BrO_4, CNS, NO_2, BrO_3, $Fe(CN)_6^{3-}$	S7	M7	Ascending technique; run 15 cm; qualitative separations by TLC and PC	117
I, IO_3, ReO_4, $Cr_2O_7^{2-}$	S8, S16 S53	M8	Adsorption of inorganic anions on Sephadex gels	118
Polyhedral borane anions	S9	M9	Ascending technique; silica gel strips stored in a bell jar containing a saturated solution of sodium nitrite	119
I, IO_3, IO_4, Te(IV), Te(VI)	S10	M10	Run 10 cm; TLC study of the separation and distribution of the chemical forms of ^{131}I produced by thermal neutron-irradiated tellurium compounds	120
Ortho, pyro and tripolyphosphates	S11	M11	Separation and identification of various phosphates	121
SCN, SO_4^{2-}, $S_2O_6^{2-}$, $S_2O_8^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	S12	M12	Ascending technique; S-chamber; layer thickness 90 mm; run 2–2.7 h; separation of H_2SO_4 from $H_2S_2O_6$	122
F^-, Cl, Br^-, I	S13	M13	The hR_F values and detection limits of halides were: F^- (6, 1 mg), Cl (25, 2 mg), Br (50, 8 mg), I (72, 2mg)	123

Table 1 (continued)

Anions	Stat phase	Mobile phase	Comment	Ref
NO_2, NO_3	S14-S27	M14	Identification and semiquantitative determination of NO_2	124
I, IO_3, IO_4, SO_3, SO_4^{2}	S15	M15	*Ascending technique, run 7 cm,* application of TLC to radiochemical inspection of ^{131}I and sulfite ^{35}S	125
I, Br, Cl, CNS, IO_4, BrO_4, ClO_4, IO_3, BrO_3, ClO_3	S16, S53	M16	Adsorption of inorganic anions on Sephadex gels	126
Polyorthophosphates (mono- to octo-)	S17	M17	Relationship between the chromatographic behavior and the structural limits of polyorthophosphates	127
F^-, Cl, Br, I, IO_3, IO_4, BrO_3, ClO_2, ClO_3, ClO_4, SO_4^{2}, SO_3^{2}, S, SiO_3^{2}, SCN, $Fe(CN)_6^{3}$, $Fe(CN)_6^{4-}$, $Cr_2O_4^{2}$, $Cr_2O_7^{2}$, NO_3, NO_2, PO_4^{3-}, WO_4^{2}, MoO_4^{2}, VO_3, VO_4^{3-}, AsO_2, AsO_3^{3-}, SeO_3^{2}, SeO_4^{2}	S18	M18	Ascending technique, run 10 cm, R_F values increase with increasing anion radius	128
AsO_4^{3-}, AsO_3^{3-}, PO_4^{3-}, CrO_4^{2}, $Cr_2O_7^{2}$, IO_3, SO_4^{2}, SO_3^{2}, S_2O_3, oxalate tartrate, F^-	S19	M19	Study of the effect of solvent composition on the separation and identification of anions	129
NO_2, NO_3, ClO_3, BrO_3, S, SCN, CN, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$,	S19	M20	Qualitative analysis of anions, layer thickness 500 mm, development time 1 5–3 h	130
Cl, Br, I, ClO_3, BrO_3, IO_3	S20	M21	Qualitative separation, optimum anion concentration (0 5–1%)	131
F^-, Cl, Br, ClO_2, ClO_3, ClO_4, BrO_3, IO_3, IO_4, SO_3^{2}, SO_4^{2}, PO_4^{3-}, BO_3^{3-}, NO_2, NO_3, SiO_3^{2}, $B_4O_7^{2}$	S17	M22	Qualitative separations of halide ions and oxy-anions	132
Various phosphates	-	-	Study of the influence of cations on the separation of phosphates	133
Bisarene chromium iodides (BCI)	S21	M23	The effect of silica gel structure on the separation of BCI	134
Twenty-five organic and inorganic anions	S22, S19	M24	Sensitive detection of anions with various detection reagents	135
ClO_2, ClO_3, ClO_4, BrO_3, IO_3, IO_4, SO_4^{2}, PO_4^{3}, BO_3^{3}, $B_4O_7^{2}$, SiO_3^{2-}, NO_2, NO_3, CrO_4^{2}, $Cr_2O_7^{2}$	S23	M25	Development in a saturated chamber, run 10 cm, TLC of organic sulfates, nitrates, and phosphates	136
CN, SCN, $Fe(CN)_6^{3}$, $Fe(CN)_6^{3}$	-	M26	Separation and detection of anions	137
Br	S5	-	Quantitative TLC determination of Br residues in crops	138
I, IO_3, IO_4,	S5	M27	Examination of effects of the nature of the alcohol, volume ratio of alcohol and aqueous ammonia, and concentration of ammonia in the mobile phase on the separation efficiency of anions	139
PO_4^{3-}, MoO_4^{2}, TeO_4, RuO_4^{2}, TeO_3^{2}, I	S5	M28	A correlation between dielectric constants of eluent and R_F values of anions is reported	140
Some anions	S24	M29	Ascending technique, run 11 cm, qualitative separations, microgram *separation of Cr(VI) from several* ores and alloys	141
$Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, MnO_4, $Mo_7O_{24}^{6-}$, $S_2O_8^{2}$, $S_2O_5^{2}$, SeO_3^{2}, SeO_4^{2}, WO_4^{2}, $Cr_2O_2^{2}$, $Cr_2O_7^{2}$, VO_3, BrO_3, IO_4, ClO_2, ClO_3, ClO_4, NO_2, NO_3	S25	M30	Paper electrophoresis, qualitative TLC and densitometric determination of anions using diphenylamine as spray reagent, detection of NO_3 and $Fe(CN)_6^{3-}$ in molasses	142

Table 1 (continued)

Anions	Stat phase	Mobile phase	Comment	Ref
Cl, Br, NO_3^-, SCN, I	S5	M31	Qualitative separations	143
Twenty-two anions including CN	S13	M32	TLC of 22 anions and 25 cations, detection of CN as $Hg(CN)_2$	144
Polyphosphates	-	-	Determination of condensed phosphates in commercial liquid polyphosphate fertilizers	145
SCN, selenocyanate	S14	M33	Detection and micro-determination of anions by densitometry	146
I, Br, Cl, SCN, ClO_3, BrO_3, IO_3, NO_2, $S_2O_3^{2-}$, SO_4^{2-}, CrO_4^{2-}, PO_4^{3-}, AsO_3^{4-}, AsO_4^{4-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	S5	M34	Chromatography on thin rods coated with silica gel	147
BrO_3	S5	M35	Detection and recovery of BrO_3 from flour, dough, and breads by TLC	148
$Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$	S14, S28	M36	Quantitative separation and recovery of anions from bleach and fixer solutions	149
Cl, Br	S5	M37	TLC detection of Br in tissue samples, in the presence of Cl, by peak area measurement, results are linear for 0 02–0 5 mmolar Br	150
NO_3	S25	M38	Densitometric determination of NO_3	151
Phosphate, silicate	S5	M39	Determination of phosphate and silicate as their molybdate complexes	152
PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$	S17	M40	Detection of phosphate on cellulose layers in the presence of molybdenum	153
Twenty-six anions	S17	-	Qualitative separations on cellulose-coated microscope slides	154
Cl, Br, I, IO_3, ClO_4, BrO_3, SCN, MnO_4^{2-}, NO_3, OAc, $Cr_2O_4^{2-}$, AsO_3^{3-}, AsO_4^{3-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	S29	M41	Qualitative separations and identification of anions	155
Monofluorophosphate	S17	M42	Detection of monofluorophosphate in extracts of toothpastes, cellulose layers	156
NO_3	S5	-	Detection of NO_3 in food and water samples, fifty five cations or anions do not interfere with detection	157
NO_2	S5	M43	TLC and densitometric determination of nitrite in saliva	158
Br and I	S30	M44	TLC detection of Br in the presence of I	159
I, Br, F^-, IO_3, BrO_3, NO_2,	S14, S31	-	Qualitative separations	160
Phosphates	S32	M45	Identification and determination of phosphates in dairy products	161
Polyphosphates	S17	M46	Detection of polyphosphates in fish products	162
Polyphosphates	S17	M47	Densitometric determination of polyphosphates in meat products	163
IO_3, IO_4, I, BrO_3, CNS, oxalate AsO_4^{3-}, PO_4^{3-}, $S_2O_3^{2-}$	S14, S33	M48	Rapid microgram determination of ferricyanide (1–4 mg) and dichromate (2–10 mg) ions	164
NO_2, I, IO_3, S^{2-}	S17	M49	Detection of anions at the nanogram levels under UV light	165
I, Br, I, IO_3, IO_4, CH_3COO, NO_3, SCN, BrO_3, MoO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, $S_2O_3^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	S14	M50	Acetone, ethyl methyl ketone, acetophenone, butan-2-ol, and formic acid - ketone systems were most suitable for providing compact and clear separations	166

Table 1 (continued)

Anions	Stat phase	Mobile phase	Comment	Ref
CInorganic phosphates	S17	M51	Qualitative separations	167
Br, I, VO_3, NO_3, NO_2, SCN, CrO_4^{2}, $Cr_2O_7^{2}$, WO_4^{2}, MoO_4^{2}, PO_4^{3}, $Fe(CN)_6^{3}$, $Fe(CN)_6^{4-}$	S14, S34	M52	Aqueous sodium chloride - acetone, aqueous ammonia - acetone (9 + 1) were the most effective solvent systems for differential migration of anions	168
IO_3, IO_4, BrO_3, I, MoO_4^{2}, $Fe(CN)_6^{4}$	S5	M53	Effect of heavy metals on the chromatographic separation of periodate from iodate, bromate, iodide, molybdate, and ferrocyanide	169
Eighteen anions	S10, S35	M54	Investigations of the effect of transition metals on the separations Cl - Br - I and NO_2 - NO_3	170
Seventeen anions	S36	M48	Qualitative separations	171
I, Br, NO_2, IO_3, BrO_3, NO_3, VO_3, MnO_4^{2}, SCN, CrO_4^{2}, $Cr_2O_7^{2}$, WO_4^{2}, MoO_4^{2}, oxalate, PO_4^{3}, $Fe(CN)_6^{3}$	S37	M55	Microgram detection and separation of anions	172
Some anions	-		Use of acid phosphates for detection and determination of typical anions	173
Some anions	S14, S10 S19, S35	M53	Qualitative separations, effect of $CaCl_2$, $MgCl_2$, and $NaHCO_3$ on the separation of anions, identification of NO_2 in artificial seawater	174
Cl, Br, I, ClO_3, ClO_4, H_2PO_4, NO_2, NO_3, SCN, SO_4^{2}	S3	M56	Separation of inorganic anions as diantipyrilmethane (DMA) complexes and salts of protonated DMA using radial or ascending technique, determination of anion content by planimetry using calibration plots of zone area against amount of anion	175

[a)]The stationary and mobile phases used are listed in Tables 4 and 5, respectively A list of abbreviations is given in Table 6

Table 2

TLC of complexes[a)]

Complex	Stat phase	Mobile phase	Comment	Ref
Diethyl thiocarbamates of Bi, Cu, Co, Ni	S14	M57	Run 20–30 min, plate activation at 110–120°C for 30 min	176
Monothio-*b*-diketonates $Rh(STTA)_3$, $Co(STTA)_3$, $Cu(STTA)_2$, $Pd(STTA)_2$, $Ni(STTA)_2$	S26	M58	Ascending technique, run 10 cm, good separations of metal chelates by elution with $CHCl_3$, limit of determination is 10 ng for Co and 50 mg for Cu, Ni, Rh and Pd	177
D and L isomers of tris ethylenediamine Co(III) complexes	S39	M59	TLC of optically active complexes	178
STTA and its metal chelates	S40	M60	Ascending technique, run 10 cm, separation of Co, Ni, Cu, Zn, Hg, Pb and Cd as their STTA, chelates, semiquantitative determination of Ni(STTA) by spot area measurement	179
Sulfate complexes of Pt, Pd, Rh, Ir	S41, S42, S43	M61	Ascending technique, run 7 cm, *TLC of the noble elements and* their sulfate complexes	180

Table 2 (continued)

Complex	Stat. phase	Mobile phase	Comment	Ref.
$Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(en_2dip)_3^{3+}$, $Co(en_2ophen)_3^{3+}$, $Co(enophen_2)_3^{3+}$, $Co(dip_3)_3^{3+}$, $Co(dip_2ophen)_3^{3+}$, $Co(ophen)_3^{3+}$	S1, S43, S44	M62	TLC of cobalt(III) complexes on alumina and silica gel	181
b-Diketonates of Fe, Cr, and Co	S45	M63	Ascending technique; run 12 cm; separation of *b*-diketonates and their metal chelates	182
2,2-Dihydroxy-5,5-dimethyl-azobenzene complexes of V, Co, Cr, Cu, Ni and Mn	S14	M64	Plate development in saturated chamber	183
Oligomers of chlorocyclophos-phaenes (tri-, tetra-, penta-, hexa-, hepta-, octa-, *etc.*)	S14	M65	Run 1 h; qualitative analysis	184
Tetraphenylporphyrin (TPP) complexes of Cd, Hg, Pb, Rh, Mn, Fe, Co, Ni, Cu, and Zn	S46, S14 S10	M66	TLC development at room temperature; run 15 cm; separation of trace metals	185
Complexes of Y, La, Pr, Sn, Dy, Nd, Sm, Gd, with the *p*-dimethyl-aminoanil of 4-hydroxy-1-naphthyl-glyoxal and the *p*-dimethylaminoanil of 4-acetyl-1-naphthol	S47	M67	Development time 0.5 to 4.5 h;	186
Xanthates of Cu, Ni, Co, Mo, Bi, Pb and Zn	S14	M68	Ascending technique; run 10 cm	187
Diphenylthiovioluric (DPHTV) acid chelates of Ni, Co, Cu, Fe, Pd, Pt and Ru	S14	M69	Ascending technique; run 15 min; qualitative separations	188
Mixture of $HgCl_2$ and ethyl mercury chloride	S14, S42	M70	Run 10 cm	189
Dithizonates of Hg, Ag, and traces of Cu, Bi, Zn, Co, Ni, Pb	S5	M71	Ascending technique; run 6 cm; application to hydrology and biological samples	190
Cd, Hg, Ph, Pd, Co, Ni, and Zn complexed with acetylthioacetanilide, acetylthioacetate-*p*-chloroanilide and thiodibenzoyl methane	S10	M72	Ascending technique; run 10 cm; qualitative analysis of metal chelates on alumina	191
Anil complexes of Mn, Fe, Cu, and Zn	S47	M73	Ascending technique; layer thickness 0.10 cm	192
Complexes of Cr, Mn, Fe, Co, Cu with the *p*-dimethylaminoanils of 4-hydroxy-1-naphthylglyoxal and 4-acetyl-1-naphthol	S5	M74	Ascending technique; layer thickness 0.10 cm;	193
Tris(acetylacetonato)Co(II)	S48	M75	Descending technique; use of polystyrene as an internal standard	194
Tc(V) cysteine, Tc(IV) cysteine, Tc(IV) Sn-DTPA	S29, S49	M76	Qualitative analysis of ^{99m}Tc species on silica gel and cellulose layers	195
Cu, Cd, Hg, Pb, Pd, Fe, Co, Ni, and Zn complexes with 3-mercapto-1,3-diphenyl 1,2-propenone (SDBM)	S5	M77	Ascending technique; run 10 cm; qualitative separations	196
Hg, dithizonate	S50	M78	Quantitatively determination of Hg(I) and Hg(II) by AAS	197
Cu, Cd, Pb, Pd, Co, Ni, and Zn glyoxal dithiosemicarbazone chelates	S14	M79	Ascending technique; glyoxal dithio-semicarbazone as a complexing and chromogenic spray reagent for inorganic TLC	198
Metal oxinates (OX): $Cu(OX)_2$, $Zn(OX)_2$, $Al(OX)_3$, $Ga(OX)_3$, $In(OX)_3$	S48, S51	M80	Descending technique; temperature 25 6 1°C; thin-layer gel chromatog-raphy of 8-hydroxyquinoline metal complexes	199

Table 2 (continued)

Complex	Stat. phase	Mobile phase	Comment	Ref.
OsO_2ACl_4, IrA_2Cl, $PtACl_4$, $AuACl_2$, OsO_2BCl_4, IrBCl, $PtBCl_4$, AuBCl	S47	M81	Ascending technique; run 8–10 cm; layer thickness 1 mm; temperature 32 6 2°C, quantitative separations	200
L-CdI_2, L_2-$AsCl_3$, L_2-$SbCl_5$, L_2AlCl_3 L-$ZrCl_4$	S14	M82	Ascending technique; run 20 cm; separation and identification of some metal ion complexes of ketone anils	201
Fe(III), Co(III), Ni(II), Ru(III), Rh(III), Pd(II), Os(III), Ir(III), and Pb(IV) chelates of 1-hydroxy-2-pyridinethione	S52	M83	Run 8 cm; qualitative analysis of metal chelates of 1-hydroxy-2-pyridinethione	202
Cu, Cd, Hg, Se, Pd, Pt, Au, Fe, Co, Ni, and Zn acetothioacetanilide chelates	S5	M84	Ascending technique; run 12 cm	203
$Co(gly)_3^{2+}$, $Fe(bpy)_3^{2+}$ $Fe(phen)_3^{2+}$	S19, S54 S55	M85	Ascending (run 15 cm) and descending (run 10 cm) techniques; layer thickness 250 mm	204
Mn, Co, Ni, Zn, Rh, Pd, Pt chelates of dithioacetylacetone	S5	M86	Run 10 cm; detection by natural color of complexes which disappeared during development	205
a- and *b*-Naphthylanils of methylene-glyoxal of Ti, UO_2, Au, and Hg	S47	M87	Layer thickness 1 mm; temperature 35°C; butanol - hexane - $CHCl_3$ (1 + 2 + 1) was most suitable mobile phase for the separation	206
cis and *trans* isomers of *Co(III)* complexes with 1.3-diaminopropane, 1,2-diaminoethane, 1,2-diamino-propane, glycine and *b*-alanine	*S5*	*M88*	*Qualitative separations*	*207*
Organogermanium compounds	S5, S3	-	Alcoholic 4,5-dibromo-2,3,7-tri-hydroxy-9-phenyl-6-fluorone?? and mixture 4 mL H_2SO_4, 8 mL $HClO_4$, 100 mL H_2O	208
Cu and Hg chelate with quinoline 2-aldehyde thiosemicarbazone	S5	M89	The results of separation and analysis of some standard samples	209
Transition metal benzoylacetonates and thiobenzoyl acetonates	*S10, S5* S17	-	Among the sorbents studied, hydroxy-lated silica gel gave best results	*210*
Diamminedichloroplatinum (II)	S28, S14	M90	Separation of *cis,trans*-diammined-chloroplatinum and their hydrolysis products	211
Seventeen metal DEDTC	S5	M91	Retention of the complexes is observed on hydroxylated silica gel; The N and S atoms make a large contribution to the formation of H-bonds with OH groups	212
cis and *trans* isomers of Ti, tetra-hedral and trigonal planar isomers of Hg, square planar and tetrahedral isomers of Zn with *p*-diethylaminoanil of anthraceneglyoxal and thiourea.	S47	M92	Separation of various isomers	213
Ti, Mn, Fe, Co, Cu, Zn complexed with the *p*-diethylaminoanil of anthracene glyoxal alone and along with thiourea	S47	M93	Cations of complexes were identified by means of migration rates and spectroscopic correlations	214
Piperidine-1-carbodithioates of Ni, Cu, Zn, Co, Cr, Mn, Fe	S14	-	Qualitative separations	215
Dithiocarbamates of Zn, Cd, and Hg	-	M94	The effect of the mobile phase on the migration behavior of the chelates	216
Sn, Mn, Fe, Co, Ni, Cu, Zr, Y, La, Pr, Nd, Sm, Gd, Dy as their ions and as their complexes with the *p*-dimethyl-aminoanil of 3-benzoylmethyl glyoxal (DMABC)	S56	M95	Ascending technique; layer thickness 1 mm, temperature 30 6 2°C; qualitative separations	217

Table 2 (continued)

Complex	Stat. phase	Mobile phase	Comment	Ref.
Isomeric complexes of Co(II) and Cu(II) with anil and thiourea	S57	M96	Quantitative separations	218
Trivalent metal complexes with *b*-diketones	S5	M97	The chromatographic properties depend on ligand structure. H-bonds were formed between O and OH groups	219
d Block cations complexed with anils	S14	-	Spectroscopic detection and identification; quantitative analysis	220
Square planar complexes of Pt and Pd with pyridine, hydroxylamine, triphenylphosphine, SCN^-, Cl^-, and NH_3	S29, S14	M98	Separation of *cis* and *trans* isomers	221
Phenylhydrazine-N-DTC complexes of of Ru, Rh, Pd, Fe, Co, Ni, Ir, Pt	-	M357	Some of the metal complexes are soluble in Me_2CO whereas others are not; the colored complexes are visible in daylight	222
DMSO - metal ion complexes	-	M100	Specific separation of Hg(II) from other metal ion complexes	223
Metal-8-hydroxyquinolines	-	-	Mass transfer conc. is equated in terms of separate spot areas for quantification of the conc. of each constituent	224
Cu phthalocyanine-4,4,4,4''' tetrasulfonic acid tetrakis (1-isopropyl-2,5-dihydroxyphenyl-amide)	S5	M101	Detection of complex on silica layer	225
Complexes of Ru sulfates	S5	M102	The R_F values and UV-Vis absorption tion spectra were measured for five different complexes of Ru sulfates	226
Co(II) and Co(III) acetylacetonates	S5, S10	M103	The differential migratory behavior of the compounds of different# valencies is discussed; quantitation by spectrophotometry	227
Tris(alkylxanthato) Co III complexes	S5	-	The R_F values of the complexes increase with increasing nos of alkyl groups; for homologous series there is a linear relationship between the number of C atoms and the R_M value	228
Transition metal complexes of monothio *b*-diketones	-	M104	Separation patterns discussed in terms of choice of solvent systems and magnitude of R_F values	229
Co, Ni, and Pd chelates with diselinoacetyl?? acetone	S5	M105	Quantitative analysis	230
$Co(gly)_3$, $Co(b\text{-ala})_3$, $Co(L\text{-val})_3$, $Co(L\text{-leu})_3$, $Co(bzac)_3$, $Cr(bzac)_3$	S14	M106	Ascending technique; layer thickness 0.3 mm; qualitative separation of isomers of Co^{3+} and Cr^{3+} complexes	231
Platinum complexes with ketoanils	S58	M107	Quantitative separation of platinum metal (Ru, Pd, Ir, Pt) complexes with TGDMA, TGDEA, TGBA; layer thickness 1 mm; ascending technique; run 10 cm	232
Cu^{2+}, Ni^{2+}, Co^{2+}, and Pd^{2+} complexes with tridentate ligand of salicylidine-amino benzoic acid	S14	-	Colored zones were eluted and characterized by elemental analysis and spectral studies	233
Metal acetylacetonates	S59	M108	Identification of Mn^{3+}, Fe^{3+}, and Co^{3+} acetylacetonato complexes as colored spots on silica layer	234
Isomers of Co(III) amino acid complexes	-	M109	R_F values increased with amino acid molecular weight; relatively high R_F values observed for *a* isomers; *b* isomers did not move	235
Rare-earth metal binuclear organometallic compounds	S5	M110	Correlation was established between R_F values and I.R. wavenumbers of >C=O of rare-earth metal compounds	236

Table 2 (continued)

Complex	Stat. phase	Mobile phase	Comment	Ref.
Co(III) - amino acid complexes	-	M111	The higher molecular weight amino move faster than those with lower molecular weights	237
Twenty complexes of Cr(III), Co(III), Ru(III), Rh(III), Fe(II), Co(II), Ni(II), and Zn(II) containing ligands such as ethylene diamine-*N,N*-diaceto-*N,N'*-di-3-propionate, ethylene propionate, 2,4-pentanedionate, 1-phenyl-1,3-butadionate or *a*-dipyridyl	S5, S10	M112	The adsorption separation mechanism of anionic and neutral complexes is explained on the basis of the polarizing power of the central ions of the complexes	238
Thiocyanate complexes of Re, Mo, V and W ions	S10	M113	Qualitative separations, TLC data can be used to determine the optimum concentrations for promoting effective complex formation in solution	239
Metal chelates	S5	-	The dependence of R_F values is explained on the basis of ion exchange of metal chelate for the H atom of the silanol groups and the dissociation of the chelates in the stationary phase	240
Seven pairs of cationic complexes and three pairs of neutral cobalt *cis,trans* isomeric complexes	S60	M114	The *trans* isomers have higher R_F values than the *cis* isomers	241
Hydroborate organometallic complexes	S5	M115	Examination of the effect of different ionic reagents (ammonium salts, SDS, and CTAB) on the R_F values of the complexes	242
Octahedral Co(III) and Ni(II) complexes	-	-	R_F values are governed by the combined effect of the conductance and the surface tension of the mobile phase	243
Pyridylazo resorcinolates of metals as ion pairs with tri-*n*-octylamine	S61	-	Complexation and ion associations of metal ions In, Ga, Fe(III), Co in a glass column followed by TLC separation; complexes identified from their inherent colors.	244
Twenty neutral tris *b*-diketonato complexes of cobalt(III) and ruthenium (III)	S60, S62	M116	Separation mechanism of metal complexes depends upon hydrogen-bond formation, interaction of phenyl group and nonspecific interaction between metal complexes, solvent and sorbent	245
Metal chelates	S5	-	Description of simulation model	246
Acylthiourea complexes	S5	M117	Best separations of chelates with aliphatic acyl substituents were obtained on RP2 layers	247
Diantipyrylmethanates of Ti, Zr, Hf; rare-earth elements, platinum and transition metals	S25, S5	M118	Quantitative determination by scanning densitometry; spectrophotometry after isolation from the layer; Application to the analysis of steel, alloys and industrial waste samples	248
Metal dialkyldithiophosphates, diethyldithiocarbamates, and *di-n-propyl dithiophosphinates*	S63	M119	Correlation between retention and the structural characteristics of metal chelates in reversed phase TLC	249
Metal oxalato and thiocyanato complexes	S64	-	Separation and identification	250
Square planar biguanide complexes of Cu, Ni and Pd	S29	M120	Copper and palladium complexes behave differently from nickel complexes	251

Table 2 (continued)

Complex	Stat. phase	Mobile phase	Comment	Ref.
Three series of tris (*b*-diketonato) complexes of Co^{3+} Cr^{3+} and Ru^{3+} in which acetylacetonato ligands were replaced with dibenzoylmethanato ligands	S66	M98	Use of unmodified silica gel as sorbent for both normal and reversed phase TLC of metal complexes	252
Twelve facial and meridonal isomers of tris(aminocarboxylato) Co(III) complexes	S14, S29 S10	M121	Examination of simultaneous effects of geometrical isomerism and chelate ring enlargement of octahedral complexes on their R_F values	253
Octyltin compounds	-	-	TLC detection of octyltin compounds; GC-MS identification as di- and?? tri-*n*-octyltin compounds after derivatization	254
Bis-carboxyethylgermanium sesquioxide	S5	M122	Quantification by densitometry at ~~λ = 255 and~~ 366 nm	255
Diphenylthiocarbazonates of Cu, Hg, Zn, Cd, Co, and Ni	S65	M123	Determination of Cu, Hg, Zn, Cd, Ni and Co in geological exploration sample by TLC of the chelates	256
Six tris(alkyl xanthato) cobalt(III) complexes	S60	M124	Confirmation of the linear dependence between the number of carbon atoms in the ligands and the corresponding R_M value of the complexes of an homologous series	257
Organotin compounds and triphenylphosphate	S5	M125	Quantitative analysis	258
Porphyrin complexes of Cu, Zn, Ni and Pd	S66	M126	The formation of Zn(II) porphyrin complexes on HPTLC plates is chromatographically undesirable	259
Pb, Cd, Zn, Cu, Ni, Mn, and Co complexes of dithizone and diethyl dithiocarbamate	S67	M127	Best separations on RP-18 with methanol - water - acetic acid (50:30:4); application for identification of Zn, Pb, Cu, and Mn in the human placenta	260
24 mixed anionic and neutral aminocarboxylato cobalt(III) complexes containing nitro ligands	S5	M128	In general, R_F values increase with increasing concentrations of salt in the mobile phase	261
Piperidine dithiocarbamate complexes of Pb, Cd, Cu and Fe	S68	M77	Separation and spectrophotometric determination of Cu and Fe in synthetic samples and their identification in alloy samples	262
Octahedral cationic Co(III) complexes	S5	M129	The mobility of the complexes depends on the surface tension and equivalent conductance of the mobile phase	263
Complexes of Cr(III), Mn(III), Fe(III), and Co(III) with 5-chloro-2,3-dihydroxy pyridine	S5	M130	The order of R_F values was Cr , Mn , Fe , Co	264
Co(III)-1-(2-pyridylazo)-2-naphthyl complexes	S32	M131	Micellar TLC separation and densitometric determination	265
Fourteen mixed amino carboxylato cobalt(III) complexes	S60	M128	An increase in the salt content of the solvent system leads to an increase in the separation factor, *a*, between two members of an homologous series	266
Homologous series of bis(alkyl-xanthato) nickel(II) complexes	S5	M98	Influence of solvent systems on the values of the complexes and the dependence of the R_F values on the number of carbon atoms in the hydrophobic moiety	267

Table 2 (continued)

Complex	Stat. phase	Mobile phase	Comment	Ref.
Mo(IV)-amino acid coordination compounds	S5	M132	Detection limit 4mg; qualitative separation and identification	268
Zn(II) coordinated compounds	S5	M133	Best separation was on silica gel with an eluent of solvent strength 0.45; eluents of higher polarity caused spreading of the spots	269
Heavy-metal complexes with pyrene-substituted *N*-acylthioureas	S66	M123	-	270
Mixed aminocarboxylato Co(III) complexes belonging to three homologous series	S17	M128	Linear dependence between the R_M values of the complexes and mol. % of the salt in the solvent system, and between the R_M values and the number of carbon atoms in the hydrocarbon moiety of the complexes	271
Tris(*b*-diketonato) complexes of Co, Cr, and Rh	S5	M134	A linear relationship was established between the R_F values of the complexes and the number of acac ligands substituted by phacphac	272
N,N-disubstituted dithiocarbamates of Ni and Co	-	-	Examination of the effect on R_F value of solvent strength and on the amine from which the chelate is derived	273
Fourteen anionic and neutral dipeptidato cobalt(III) complexes	S5	M128	R_F values of complexes decreased with increasing mobile phase salt concentration	274
Cationic, anionic and neutral cobalt(III) complexes	S29	M135	The separations are based on outer sphere association between the complex cation and the anion present in the mobile phase; R_F values strongly depend on the charge of the complex	275

[a)]The stationary and mobile phases used are listed in Tables 4 and 5, respectively. A list of abbreviations is given in Table 6.

Table 3

TLC of metals and metal cations

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Be, Mg, Ca, Sr, Ba	S49, S70	M136	Combination of TLC and emission spectroscopy for micro-determination of alkaline earth metals; application to the analysis of ashed plant materials	276 277
Rare-earth elements and transition metals	S71, S69	M137	Conditioning time 30 min; run 13 cm; temp 25–30°C; quantitative separation of Zr(IV) and Hf(IV)	278
Radionuclides ^{90}Sr, ^{90}Y, ^{140}Ba, ^{140}La	S185	M138	Run 15 cm; separation of daughter nuclides from ^{90}Sr, ^{90}Y, ^{140}La, ^{140}Ba,	279
Ni and Co	S42, S186	M139	Estimation of the properties of silica gels by use of the separation characteristics of control mixtures	280
Tl, Al, Ag(I), Pb, Hg(II), Cd, Cu, Zn, Mn(II), Co, Ni, Ba, Sr, Ca, Mg, Be	S72	M140	Run 11–12 cm; examination of the influence of complex formation on the chromatographic behavior of inorganic ions	281
Rare-earth elements	S73	M141	Ascending technique; run 10 cm; separation of mixtures of 10–12 rare-earth elements at submicrogram levels	282

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Hg, Zn, Sb, Cd, Bi, Pb, Cu, Co, Fe, Mn, Ni	S74	M142	Run 14 cm; qualitative analysis	283
In, Sn(IV), Sn(II)	S40	M143	Ascending technique; run 10 cm; 0.25 mm layer; separation of ^{113}Sn ^{113}In by TLC	284
Cu, Co, Mo, U, V, Ti, Fe	S14	M144	Separation of metal ions by TLC with salicylhydroxamic acid as complexing agent	285
Be, Al, Ti, V(IV), V(V), Cr(III), Cr(IV), Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As(III), As(V), Se(IV), Se(VI), Y, Mo, Ru, U	S75	M145	Ascending technique; run 15 cm; selective separation of U(VI)	286
Fe, Ag, Co, Ni, Cu	S76	M146	Ascending technique; identification of Cu, Ag, Ni, Co, and Fe in sulfide chalcopyrite ore; separation of silver	287
Re, Mo, V, W	S10	M147	Investigation of the effect on R_F of composition of mobile phase containing salicylic or sulfosalicylic acid and different concentrations of NaOH or HCl	288
Th, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc	S19, S187	M148	Ascending technique; run 6.5–7.5 cm; mobility of metal ions on microcrystalline cellulose	289
Rh, Pd, Pt, Au	S77	M149	Ascending technique, temp. 70°C; run 8–30 min, chromatographic behavior of noble metals in chloride systems by paper chromatography and TLC	290
Ge, As(III), As(V)	S29	M150	Ascending technique; run 10 cm; 0.25 mm layers; separation of ^{77}As from the parent nuclide ^{77}Ge in a carrier-free state	291
Hf, Zr, U, Th	S78	M151	Ascending technique; run 170 mm; separation of Zr, Hf, Th, U and rare-earths on DEAE-cellulose in sulfate media	292
Ti, Ge, As, Se(IV), Se(VI), Te(IV) Te(VI), Ag, Sn(IV)	S4	M152	Ascending technique; run 15 cm; chromatography of a number of inorganic ions on DEAE - cellulose layers with formic acid media	114
Cu, Pb, Al, Fe, Zn, Ca	S79	M153	Run 10 cm; temp. 25 6 1°C	293
Sc, Zn	S188	M154	Ascending technique; run 7 cm; determination of Zn in the presence of Cd by TLC separation and activation analysis	294
Rare-earth elements, transition metals and nonmetals	S78	M155	Ascending technique; run 17 cm; TLC of several metal ions on DEAE - cellulose in acidic sulfate media	295
^{51}Cr(VI), Al	S5, S10	M156	Ascending technique; run 90 min; determination of the radiochemical purity of radiochromate solution	296
Re, Mo, W, V	S80	M157	Ascending technique; separation and identification of Re, Mo, W and V on thin layers of diatomite	297
Rare-earths, transition metals and Bi	S81	M158	TLC behavior of metal ions on Ecteola cellulose with hydrochloric acid media	298
Rare-earths, transition metals and nonmetals	S82	M159	Ascending technique; run 11 cm; TLC of 47 metal ions on an inorganic ion exchanger with mixed solvent systems	299

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Am, Ni, Pb, Fe, U, La	S83	M160	Ascending technique; run 10 cm; saturated chamber; adsorption behavior of americium in the system nitrate solution - silica gel - amine	300
47 inorganic cations	S14	M161	Ascending technique; run 10 cm; quantitative separation of Cd^{2+} and Cu^{2+} from other metal ions	301
Rare-earth elements, transition metals and nonmetals	S189	M162	Ascending technique; chamber pre-equilibrated for 1 h; run 15 cm; TLC separation of inorganic ions	302
Rare-earth elements, transition metals and Be^{2+}	S84	M163	Ascending technique; run 11 cm; TLC of 49 metal ions; quantitative separation of uranium from numerous metal ions	303
La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb, Lu	S190	M164	Layer thickness 0.1–0.25 mm; qualitative separations	304
Ru, Rh, Pb, Pt, Au	S14	M165	Ascending technique; development time 20 min, evaluation of Ru, Rh, Pd, Pt, and Au by ring colorimetry	305
Ni, Mn, Co, Cu, Fe, Zn, Al, Cr	S19	M166	Ascending technique; run 10 cm; layer thickness 0.2 mm	306
Sn(II), Sb(III), Pb	S19, S85	M167	Air-free atmosphere; run 14 cm; 2,2-diquinoxalil as a new reagent for determination of bivalent tin	307 308
Re	S191	M168	Ascending technique; study of the behavior of perrhenate in acetic acid solution by TLC and infrared spectroscopy	309
Cu, Ag, Cd, Hg, Tl(I), Pb, Bi, As(III), Sb(III)	S86	M169	Plate development at 30 6 1°C	310
Cu, V, Cr, Mn, Fe, Co, Ni, U, Li, K, Rb, Mg, Ca, Sr, Ba	S86, S192	M170	Separation on EDTA impregnated plates	311
Twenty-six metal ions	S82	M171	Ascending technique; run 10 cm; quantitative separation of Hg(II) from Cd(II), Zn(II) and Cu(II)	312
Rare-earth elements and transition metals	S87	M172	Ascending technique; run 17 cm; TLC of several metals on cellulose phosphate with phosphoric acid media	313
La, Ce, Pr, Nd, SM, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	S88	M173	Qualitative analysis of lanthanide metals on 0.1–0.25 mm Polygram plates with different solvent mixtures	314
Be, Mg, Ca, Sr, Ba	S19	M174	Ascending technique; run 10 cm; layer thickness 0.25 mm, TLC separation of alkaline earth metals	315
Cu, Cd, Fe, ~~Al~~, La, Pr, Nd, Sm Au, Mn, Zn, Cr, Al, Pt, Au, Hg, Tl, In	S89	M175	Ascending technique; run 10 cm; quantitative separation of gold from numerous metal ions	316
Mg, Ca, Sr, Ba	S90	M176	Separation of by circular TLC	317
Eighteen metal ions	S91	M177	Qualitative separation	318
Rare-earth elements and transition metals	S92	M178	Ascending technique; run 10 cm; quantitative separation of Cr(III) from numerous metal ions	319
Cu, Ag, Hg, Pb, Sb(V), AI, Ti, V(V), Fe, Co, Ni, Zn	S93	M179	Ascending technique, qualitative separations	320
Os, Pt, Pd, Au, Ir, Fe, Cu, Ni, Rh	S193	M180	Ascending technique; run 12 cm; separation of Pt metals	321
Au, Ir(IV) (~~XV~~), Pt, Pd, Ru, Rh, Ir(III)	S94	M181	Ascending technique; 0.25 mm layer; run 10 cm; separation of noble metals on diethylaminoethylcellulose with aqueous chloride solutions	322

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Ir(IV), Rh(III)	S94	M182	Layer thickness 20 mm, dry in air for 1 h before drying at 40°C for 4 h; store in tank over saturated KBr solution; selective separation of rhodium and iridium	323
Cu, Ag, Hg, Pb, Bi, Fe(III), Co, Ni, Zn	S14	M183	Ascending technique; run 12 cm; quantitative separation of Fe^{2+} and Hg^{2+}; elution with 0.05 M H_2SO_4 from silica gel then spectrophotometric determination using 1,10-phenanthroline and dithizone, respectively, as color reagents	324
Cu, Ag, Cd, Hg, Tl(I), Pb, Mn, Co, Ni, Zn, Mg, Ca, Sr, Ba	S95	M184	Ascending technique; run 11 cm; chromatographic behavior of inorganic ions on thin layers ~~chitosan~~ and columns of chitosan.	325
Pb, Zr, Sn, Ti, Zn, Al, Tl, Ag, Cu, Hg, Be	S96	M185	Qualitative separations	326
Twenty four metal ions	S97	M186	Ion exchange TLC of metal ions using mixed aqueous organic solvent systems	327
Fifty elements	S17, S98	M187	Se-Te, In-Ga, Zr-Hf separations	80
Cu, Hg, Pb, Bi, As, Mn, Fe, Co, Zn, Mg	S19	M188	Detection and semiquantitative determination of metals, present as components or impurities in pharmaceutical products	328
Cu, Ag, Cd, Hg, Pb, As, Sn(IV), Sb, Sc	S99	M189	Separation on diethylenetriamine-impregnated layers	329
Se, Te, Au	S10	M190	Run 10 cm; for complete separation using 0.1–6 N NaOH as mobile phase it is necessary to treat the layer with 0.1 M HCl before development	330
Cu, Ag, Cd, Hg, Pb, Pd, Co, Ni, Zn	S71	M191	Ascending technique, glyoxal dithio-semicarbazone as a complexing and chromogenic spray reagent in inorganic TLC	198
Eighteen cations	S100	M192	Binary and ternary separations	331
Be, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sb, Mo, Cd, Sn(II), Sn(IV), Ba, Hg, Tl, Pb, and Bi	S101	M193	Binary and ternary separations	332
Twenty four metal ions	S102	M194	Qualitative analysis of metal ions	333
As, Sn, Co, Cd, Fe, Al, Ni??, Pb, Cu, Zn, and Sb	S103	M195	Qualitative separations	334
Fifty one inorganic ions	S104	M196	Qualitative separations, best results with acid sulfate solution as eluent	335
Several metal ions	S105	M75	Qualitative separations and quantitative estimation of Hg(II)	336
Several metal ions	S106	-	Quantitative separation of Hg(II)	337
Mn, Fe, Co, Ni, Cr, As, Sb, Th, U, V^{5+}, Se, Mo	S194	M197	Qualitative separations	338
Ag, Te, Cu, Hg, Be, Zn, Pb, Mn, Fe, Co, Ni, Al, As, Sb, Cr, Th, Zr, Sn, Ti, V, U, Mo, Se	S195	M198	Qualitative separations	339
Rare-earth metals		M199	Separation of La, Ce, Pr, Nb, Pm, Sm, Eu, and Y	340

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Rare-earth metals	S5	M200	Two-dimensional TLC to separate lanthanides and HPLC to separate nine rare-earths using columns packed with silica gel	341
Mo, W	S107	M201	Separation of molybdenum and tungsten from rare-earths	342
Rare-earth metals	-	M202	Separation of all rare-earths and of one rare-earth from all others in a ratio of 8000:1	343
Cd	S19	M203	Developed in a solvent-vapor-saturated atmosphere; run 15 cm; 0.1 mm layer; estimation of Cd ion by fluorescence scanning	344
Cu, Ag, Cd, Hg, Pb, As, Sn(IV), Sb, Se, Se(IV), Al, Cr(III), Fe(II), Co, Ni, Zn	S108	M204	Separation of inorganic ions; temp. 30 6 1°C	345
Ba, Sr, Te, La, Ce, Pr, Nd, Pm, Sm, Eu, Y, Tc, Mo, Zr, U	S88	M205	Two-dimensional development; qualitative analysis of lanthanides on 2 mm silanized silica gel layers	346
Cu, Zn, Ni	S109	M206	Saturated chamber; run 10 cm; a relationship between the ion-exchange constant and experimental R_F values was derived, to enable transfer of the theoretical approaches developed for column ion exchange chromatography to TLC	347
Forty-nine ions including W, Ha, Tl, Mo, Re, Sn, Pb, Cr, Ni, Cd, Zr, Co, Cd, Te, Sc, Sb, Cu, Ag, As, Be, Fe, Mg, Th, Y, Ge	S110	M207	Development time 35–45 min; layer thickness 0.25 mm; run 17 cm; qualitative separations	348
Bi, Th, Zr, Ce, Cr, Al, Ti, W, UO_2, Sn, Fe, Sb, V	S29	M208	TLC-photometric method for separation and determination of micro amounts of Mo(VI) in the presence of interfering cations	349
Eighteen metallic ions	S5	-	Identification and separation of inorganic cations	350
Cations	S5, S17	M209	Qualitative separations	351
Forty-eight metal ions	S14	M210	Qualitative separations	352
Rare-earth metals	-	M211	Separation of rare-earth metals in ores (monazite), rocks, pure $Ce(NO_3)_n$, and irradiated nuclear fuels, separation of rare-earths from uranium	353
V, Th, As, Pb, Zr, Se	S99	-	A correlation between R_F values of metal ions on impregnated layers and the stability constants of the metal in the impregnant is discussed	354
Twenty-two cations	S29, S19	-	Qualitative analysis	355
Twenty-three metal ions	S111	M212	Binary and ternary qualitative separations	356
Inorganic metal ions	S19	M213	High loading blurs the separation of cation mixtures	357
Group I, IIA, IIB, and IIIB cations	S112	M214	EtOH - $CHCl_3$ - HCl and BuOH - $HCONH_2$ solvent and systems give best results	358
Several metals ions	S113	M75	Quantitative separation of microgram quantities of Hg(II) from several other metal ions	359
Rh(III), Ir(III), Ir(IV)	S102, S115	M215	Separation by anion exchange TLC	360

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Ni, Mn, Co, Cu	S114	M216	Separation on silica gel was poor; addition of ion exchange resin markedly improved the resolution	361
Au, Ir(III), Ir(IV), Pt, Pd, Ru, Rh	S115	M217	Qualitative separations	362
Rare-earth metals	S88	M218	Separation and detection of rare-earth metals in a variety of mixtures	363
Forty metal ions	S116	M219	Qualitative analysis	364
Transition metal ions	S14	M220	Separation of Fe(III), Ce(IV), Cu(II), Co(II), Cr(III), and Ni(II)	365
Rare-earth metals	S88	M221	Qualitative separations	366
Mo, Y, La	S5, S196	M222	Chromatographic behavior of La, Y and Mo was investigated.	367
Ni, Cu, Hg, Pb, Bi, As, Ce, Tl	S17	M223	Separations on the basis of differential solubilization of metal chloro complexes	368
Cr(III), Cr(VI)	S28	M224	Optimum conditions for quantitative separation of Cr(III) and Cr(VI) from their binary mixtures	369
Hg, Cu, Cd, Ag	S14	M225	Concentration, separation and detection of microgram amounts of Cu, Ag, Hg, and Cd salts in fresh water	370 371
Cd, Bi, Hg, Pd, Pt, Th, As, Ru, Pb, Te, Sc, Ag, Ge, Sb, Zr, W, Re, Sn, Tl, Zn Mo, Cr, UO_2	S118	M226	Ascending technique; run 17 cm; development time 40–60 min, layer thickness 0.5 mm	372
Cu, Hg, Zr, Zn, Cr, Y, Gd, Ho, Nd, La, Pr, Ce, Pd, Au, Pt, Co, Ni, Fe, Bi	S119	M227	Spectrophotometric determination of Pd^{2+}, after elution from the TLC plate, using *p*-nitrosodimethylaniline as chromogenic reagent	373
Zr, Ce, W	S5	M228	Quantitative separation of Zr^{4+} from lanthanum and Ce^{3+}; W^{6+} from Cr^{3+}, Mo^{6+}, and vanadyl (V^{2+})	374
Twenty-five cations	S17	M229	Development time 15–25 min, TLC on microscope slides	375
Rh(III), Ir(III), Ir(IV)	S102, S115	M230	Anion exchange separations	376
Gold, selenium, tellurium	S5, S10, S120	M89	Separation, detection and determination of micro amounts of Au(III). Se(IV), and Te(IV)	377
Fe, As, Sb, Hg, Sn, Cr	S121, S49	M231	Separation of different valency states	378
Rare-earth elements	S122	M232	Separation and spectrophotometric determination of rare-earth elements; application to the determination of La, Ce, Pr and Nd in monazite	379
Ba, Y, La, Ce	S197	M233	Quantitative separation from Sr	380
Forty-seven metal ions	S82	M234	Qualitative separations and adsorption behavior	381
Nineteen metal ions	S5, S123	M235	Detection limits of metal ions on plates was 1.0–7.0 mg	382
Cu, Zr, Gd, La, Au, Pd, Hg, Pt, Y, Ho, Nd, Pr, Ce, Co, Zn, Fe, Bi, Cr	S119	M236	Ascending technique; run 11 cm; layer thickness 0.1 mm; air dried at room temperature for 3 h; development time 6–10 h	373
Pb, Mn, Zn, Cd, Ni, Co, Cu, Fe, Mg, Pd, V, UO_2, Th	S5, S124	M237	Dibenzoyl methane impregnation offers a method for the removal of iron from silica gel G	383
Forty-nine inorganic ions	S104	M238	Qualitative separations	384
Forty-eight metal ions	S14	M239	Qualitative separations	385

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Lanthanides	-	M240	HPLC and TLC excellently supplement each other in the separation of lanthanides; application to the separation of fission products	386
Ni, Ca, Cu, Mn	S125	M241	Preparation of stationary phase and its application in inorganic TLC	387
Rare-earth elements	S122	M242	Separations of La, Ce, Pr, Nd, Sm, Eu, Th, and Ho	388
Ti, Zr, AsO_4^{3-}, MoO_4^{2-}, Th, Al, Cr, Fe, Ce, VO_3^-, Be, Bi, Ni, UO_2, Co, Cu, Hg, Pb, Mn, Zn, Cd, Sb, Sn	S29	M243	Ascending technique; conditioning time 10 min; development time 15–20 min; layer thickness 0.25 mm; plate activation at 120°C for 1 h; quantitative separation of Zr and Ti from each other and from other interfering ions	389
Cu, Cd, Zn, Ni, Co, Fe, Pb, Cr, Al, Zr, V, Th, Cd, UO_2^{2+}, Ag, Se, VO^{2+}	S5, S126	M244	Ascending technique; run 10 cm; development time 12–15 min, 0.25 mm layer, semiquantitative determination of nine cations on silica gel impregnated with sodium molybdate	390
Dy, Gd, Nd, La, Pr, Tb, Sm, Th, Ti, Zr, and some rare-earths	S5, S127	M245	Ascending technique; run 12 cm; 0.5 mm layer; impregnant concentration (1%) in EtOH - H_2O (70:30); plates dried for 24 h at 40 6 1°C; development temperature 22 6 1°C	391
Pb, Cd, Hg, Te, W, Mn, Ag, Fe, Be, Ni, Mg, Pt, Ga, Cu, Ti, Se, Fe, Co, As	S128	M246	Ascending technique; run 17 cm; development time 60–80 min; 0.25 mm layer; qualitative separations	392
Pb, Mg, Ca, Cd, Zn, Fe, Mn, Hg, As, Th, Fe(II), UO_2 (II), V(V)	S129	M247	The impregnated silica gel plates were activated at 60° 6 1°C for 24 h; run 10 cm	56
Se, Te, and Au	S10	M248	Plates developed in Stahl chamber	393
Bi, Au, Mn, Co, Zn, Ti, Cu, Ag, Ni, Pt, Cd, Pb, Hg, Tl(I)	S130	M249	Ascending technique; run 11 cm; development time 2 h; quantitative separation of Bi^{3+} from some ternary and quaternary mixtures of metals	394
VO^{2+}, Fe, Al, Fe^{2+}, UO_2^{2+}, Bi, Tl^+, Mo, Cd, Cu, Pb, Zn, Co, Th, Se, W, Zr, Cr	S131	M250	Ascending technique; run 10 cm; development time 15–20 min; butylamine-impregnated silica gel layers were selective for metal ions at lower mobile phase pH values (pH 1–2.5) whereas *t*-butylamine-impregnated silica gel layers were more selective at higher mobile phase pH values	395
Rh(VII), Mo(VI), V(V)	S10	M251	Study on the effect of nature and composition of the mobile phase on the chromatographic behavior of Ru, Mo and V	396
Rare-earth metals	S5	M252	Continuous separation of rare-earth metals, La, Ce, Pr, Nd; detection of Sm in monazite sand	397
Fe, Pb, Co, Zn, Cd, Cu	S122	M253	Qualitative separations	398
High valence metal ions	S132	M254	Separation of binary and ternary mixtures of rare-earths, Ti(IV), Zr(IV), Nb(V), and U(VI)	399
Alkaline earths and transition metals	S133	M255	Separation of Ca^{2+}-Sr^{2+}, Ca^{2+}-Ba^{2+}, and Hg^{2+} from Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+}	400

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Noble metals	S134	-	Separation of noble metals from commonly present metals	401
Co, Cu, Ni	S135	M117	Separation and detection as DEDTC	402
Thirty-six cations	S29	M256	Qualitative analysis of 36 common cations	100
Fe, Fe^{2+}, Zn, Cd, Ni, Co, Cu, Pb, Hg, Al, Tl^{+}, W, UO_2, Se, Nb, VO^{2+}	S14	M257	Most effective concentration range of HCOOH in butanol was 5.0 -20 M; The presence of ethylmethyl ketone in the HCOOH - butanol system improves the resolution of the separation	403
Y, Sm, Nd, Pr, Ce, La, Lu, Yb, Tm, Er, Ho, Dy, Tb, Eu, Gd	S12	M258	Ascending technique; development time 20 min for 10 cm run; 250 mm layer; plate activation at 70°C for 20 min, sample volume 0.5 mL	404
Cu, Fe, Mn	S19	M259	Separation and detection of Cu, Fe, and Mn in cotton materials (lower limit 20 mg g^{21} material)	405
Ag, Al, As, Au, Ba, Be, Bi, Ca, Ce, Ce^{4+}, Co, Cr, Cu, Dy, Fe, Ga, Ge, Hg^{+}, Hg, Ln, La, Lu, Mg, Mn, Mo^{6+}	S136	M260	Qualitative separations on treatment with PEI-cellulose	406
Al, Ni, Cr, Mn, Co, Zn, Fe	S137	M261	Ascending technique; development time 3 h; loading volume 2 mL of acidic extract; determination of micro elements in Polfamik products using standard curves prepared from spot surfaces of separated metal ions on TLC plates	407
Fe^{2+}, Cr, Zn, Co, Fe^{3+}, V^{4+}, Ni, Cu	S138	M262	Simultaneous separations and semi-quantitative determination of several transition metals according to the color reaction appearing in the sorption zone of the element on the plate; semiquantitative determination of Ni, Cu, and Cr in waste waters	408
Ag, Al, Cu, Th, Mo Zn, Cd, Pb, Se, Zr, Ni, W, UO_2^{2+}, VO^{2+}, Fe, Tl^{+}, Co	S139	M263	Semiquantitative determination of Pb, Ag and Th by spot area measurement method and spectrophotometric determination of UO_2^{2+} after separation from other metal ions	409
Twenty-two metal ions	S14	M264	Semiquantitative determination of nine cations by spot area measurement method, most effective concentration range of formic acid was 0.1–1.0 M	410
Forty-nine inorganic ions	S136	M265	Ascending technique; run 17 cm; development time 100–120 min; qualitative separations	411
Rare-earths, Cd, Co, Pb, Cu, Zn, U(VI), Th	-	M266	Qualitative separations	412
Light rare-earth metals	S140	M267	Effective separation of light rare-earths in the presence of heavy rare-earths	413
Light rare-earth metals	S198	M268	Separation of light rare-earth metals in monazite	414
Mn(II), Mn(III)	S14	M269	Ascending technique; run 20 cm; layer thickness 250 mm; optimum conditions were determined for quick quantitative separation of di- and trivalent Mn as their acetylacetonates	415

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Twenty-three metal ions	S14	M270	Ascending technique; run 10 cm; development time 20 min; activation at 100 6 5°C for 3 h	416
Rare-earth elements and other metal ions	S136	M271	Ascending technique; 0.25 mm layer; run 170 mm; development time 100-110 min; correlation between R_F values and the paramagnetic moment of the rare-earths(III) is presented	417
Ru, Au, Pd, Pt, Rh, Os, Ir, Ag	S141	M272	Qualitative analysis	418
Fourteen rare-earth elements	S5	M273	The plates were first developed with solvent A, dried, and redeveloped with solvent B	419
Heavy rare-earth metals	S142	M274	Separation of Cd, Tb, Dy and Ho	420
Rare-earth elements	S143	M275	Qualitative separations of rare-earth metals	421
Pb, Fe^{2+}, Ni, Co	-	M276	Separation of metal ions from mixtures using four developing solvents	422
Transition metals	S144	-	Qualitative analysis	423
Zn, Cd, Cu	S5	M277	Separation of Zn(II) from Cd(II) in the presence of certain anions in sample solutions of different pH	424
Fe^{2+} and Fe^{3+}	S14	M278	Ascending technique; run 10 cm; development time 30 min; 0.25 mm layer; sample pH 1.3; separation of Fe^{2+} from Fe^{3+} in the presence of Cl^- Br^-, SO_4^{2-}, SO_3^-, PO_4^{3-}, and CH_3COO^- ions	425
Fe, Cd, Zn, Cu, Bi, Tl^+, Ag, Hg, Pb Hg, Pb, Se, Mn, UO_2^{2+}, Ni, Zn, Al, Zr, Ti, Th	S14	M279	Ascending technique; run 10 cm; development time 15–20 min, 0.25 mm layer; examination of effect of sample concentration, eluent concentration, pH of salt solution, pH of mobile phase, and presence of anions in the sample solution on the separation of Cd^{2+} from Zn^{2+} and of Cu^{2+} from Ni^{2+}, Co^{2+}, and Cd^{2+} with 1.0 M NaCOONa - 1.0 M KI (9:1)	426
Al, Fe^{2+} Fe^{3+}, Co, Ni, Cu, Zn, Ag, Cd, Hg, Tl, Pb, Bi	S145	M280	Ascending technique; run 10 cm; quantitative separation of Ni from Fe, Zn, Cd, and Pb	427
Ni, Co, Zn, Cd, Cu, UO_2^{2+}, V^{4+}, Fe^{2+}, Fe^{3+}, Al, Th, Ti, Mo^{6+}, Se, W, Hg, V^{5+}, Tl^+, Pb, Bi, Ag	S14, S14+ S10	M281	Ascending technique; run 10 cm; 0.25 mm layer; loading volume 5 mL; examination of the effect of sample pH, presence of anions in the sample, and the presence of alumina in the stationary phase on the separation of V^{5+} from W^{6+} and Mo^{6+}	428
UO_2^{2+} Ti, Al, W, Ni, Fe, Co, Mn, Cu, Bi, Zn, Cd, Ta, Se, Pb, Ce, Ag, Th, Zr, Hg, Tl	S146	M282	Ascending technique; run 10–12 cm, development time 1–2 h; qualitativ separations	429
Th, Zr, UO_2^{2+}	S14	M283	Ascending technique; run 10 cm; 0.25 mm layer; studies on the effect of anions on the separations Th^{4+} - Zr^{4+} - UO_2^{2+} and Th^{4+} - Zr^{4+}	430
Light rare-earths	S122	M284	La, Ce, Pr, Nd, Sm, Eu, and Gd were completely separated; detection limit 0.01 mg; rare-earth R_F values decreased with increasing atomic number	431

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Rare-earth elements	S147	M285	R_F were governed by the amount of each component in the eluent; discussion of the mechanism of separation mechanism of REE; application of the method to the separation of REEs in monazite	432
Rare-earth elements	S147	M286	Qualitative separations; detection limits 0.01 mg; increase in R_F value with increasing volume of trimethyl ammonium chloride in the mobile phase	433
Rare-earths	S5	M287	Rare-earth R_F values in the range 0.1–0.7; separation of individual rare-earths from artificial mixture and from minerals and alloy samples	434
Heavy rare earths	S140	M288	La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y are separated from each other; developer showed better separation efficiency	435
Rare-earth elements	S148	M289	Separation of rare-earths by partition chromatography; run 18 cm; studies on the effect of pH of lactate solution, methanol concentration, and temperature on the migration and resolution of the rare-earth elements	436
La, Nd, Eu, Tb, Gd, Dy, Ho, Sm Er, Tm, Yb, Sm, Pr	S149	M290	Separation of rare-earth elements in middle of atomic weight range	437
VO^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}	S5	M291	Synthesis, spectroscopy and chromatography	234
28 metal ions including Ru, Pd, W, Pt, Au, Mo, and UO_2^{2+}	S150	M292	Quantitative separation of Ru^{3+} from other metal ions	438
All rare-earths except Pm	S5	M293	Gives chromatograms showing typical separations of multicomponent mixtures containing adjacent lanthanides	439
Rare-earth elements	S151	M294	Separation of lanthanides	109
La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Y, Pb	S140	M295	Qualitative separations and applications of the method to the analysis of rare-earth ores	440
Noble metals (Rh, Ru, Pd, Pt, Ir, Au)	S158	M296	All noble metals were completely separated	441
La Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	S122	M297	Qualitative separations of rare-earths; plates were developed first with mobile phase I (ascent 8–14 cm; dried at 40°C) and redeveloped in the same direction with mobile phase II to a distance of 20 mm	442
Metal ions	S126	M298	Selective separation of TI(III) from Cd, Al, Ni, Fe, Ag, and Pb	443
Fe^{2+}, Fe^{3+}, Ni, Zn, Pb, Mn, Cu	S14	M299	Reversed phase partition TLC of metal ions and examination of the effect of chlorosubstituent groups on R_F values	444
Ni, Cu, Zn, Mn, Fe	S14	M300	Studies on the effects of plate width, acetate concentration in mobile phase, and time on the R_F values of the individual cations; best separation with 0.1 M sodium acetate; application of the method to the separation of metal ions in tube-well water samples	445

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Inorganic ions	S11	M301	Qualitative separations from multicomponent mixtures.	446
Forty-nine inorganic ions	S11	M302	The sorption of most ions increases with increasing methanol content in the mobile phase	447
Forty-nine inorganic ions	S11	M303	Selective separation of As(III) and Ti(IV) from many other ions	448
Cu in Al - Fe - Ti alloy	S5	M304	Separation of Cu in ferrotitanium by concentration gradient TLC	449 450
Al, Co, Ni, Zn, Ag, Cd, Tl, Pb, Bi, Mg, Hg, Fe, Cu	S14, S153	M305	Much shorter development time on NH_4Cl-impregnated silica gel layers; clearer detection and more compact spot formation on KI-impregnated silica gel layers; better results when KBr is used as eluant rather than as an impregnant, but reverse is true for KI; 1.0 M formic acid - 1.0 M KBr (1 + 1) and formic acid - KI (1 + 9) were the best eluents for separating Fe^{2+} and Cu^{2+} from several metal ions; quantitative separation of Tl, Al, Fe, Zn, and Cd	450
Hg^{2+}, Hg_2^{2+}, Pb, Ni, Cu	S154	M306	Recovery of Hg^{2+} from river water and industrial waste water	451
Twenty-seven cations	S155	M307	Qualitative separation; effect of pH on the R_F values of metal ions in eluents containing lactic and citric acids	452
Cu, Cd, Co, Pb	S156	M308	Quantification by densitometry, detection limit in the nanogram range; the method was applied to the determination of Cu and Pb in ground water and electroplating waste water	453
All rare-earth elements including Y	S29	M309	Qualitative separations and quantification by densitometry; detection limits in the 14–31 ng range	454
Alkali metals and alkyl xanthates	S157	M310	Method suitable for the analysis of flotation mixtures; detection limit 0.5 mg	455
Noble metals (Au, Pd, Pt, Ru, Ir, Rh)	S158	M311	Qualitative separations	456
V, Mo, W, Re	S159	M312	Effective mutual separations of V^{5+}, W^{6+}, Mo^{6+}, and Re^{7+} with 0.5 M HCl - ethanol (9 + 1) eluant; optimum activation temperature 75°C for faster development; starch as a binder causes tailing whereas dextrin, or Solvar (polyvinyl alcohol) containing 10–14% acetate groups gives better separations	457
Ag, Ni, Cu, Co, Cd, Hg	S160, S95	M313	Separation of mixtures of inorganic ions on chitin layers; possible use chitin and chitosan layers in wastewater- and sea water-purifying systems	458
Fe, Ni, Cu, Zn, Pb, Mn	S14	M314	Separation and detection of metal ions in industrial wastewater samples	459 460
Co, Ni, Mn	S161	M315	Study on the mobility of chlorides, carbonates, and sulfates of the metals was investigated	460

Table 3 (continued)

Cation/metal	Stat phase	Mobile phase	Comment	Ref
Fe, Ni, Cu, Pb, Zn, Mn	S5	M316	Examination of the effects of pH, concentration of glycolic acid, and development time on the R_F values of individual cations in adsorption and partition TLC	467
Au, Se, Tl	S10	M317	Simple and rapid separation of Au^{3+}, Se^{4+}, and Tl^{4+}	463
Ni, Cu, Cd, Co, Zn	S29	M318	TLC separation and densitometric determination of Zn, Cu, Ni, and Cd at trace levels (0 01–0 3 mg)	464
Twenty-three metal ions	S162	M319	Qualitative separations	465
Lanthanides and other elements (Ce, Nd, Sm, Gd, Ho, Yb, Y, Ti, V, Zr, Th, U)	S163	M320	Examination of the effects of the concentration of H_2MEHP and HNO_3 on the R_F values of the elements	466
Forty-nine inorganic ions	S11	M321	Separation of multicomponent mixtures of ions	467
Rare-earth metals	S164	M322	Qualitative separation by circular TLC	468
Re, Mo, W, V	S10	M323	Separation of Re^{7+}, Mo^{6+}, W^{6+}, and V^{5+} ions from their mixtures by TLC and electrochromatography, investigation of the relationship between R_F values and concn of acid in the mobile phase	469
All rare-earths except Pm	S5	M324	Separation of multicomponent mixtures containing adjacent lanthanides, discussion of the effects of solvent cations and anions on R_F values	469
Au, Pt, Pd, Cr, Mn, Fe, Co, Ni, Cu, Ba, Al, Bi, Pb, Zn, Ag	S115	M325	Application of method for the analysis of platinum powder and two kinds of Au alloy	470
Metal ions of first transition series	S165	M326	Reversed phase TLC separations of metal ions, best separations at amine concentrations of 2 and 3% in 0 03 M citric acid mobile phase	471
Cu, Fe, Hg, Pb, Co	S5, S166	M327	The mobility of metals generally increases on impregnated layers in the order phthalic salicylic syringic acid	472
Forty-nine inorganic ions	S167	M328	Qualitative separations	473
Inorganic ions	S168	M329	Selective separation of Re(VII) from many inorganic ions	473
Zr, Hf	S5	M330	Complete separation of the two metals present in Zr Hf ratios ranging from 20 1 to 1 40	475
Several metal ions	S17, S169	M331	Separation of metal ions with *different valence states*	476
Fe, Ni, Zn, Cu, Pb, Mn	S14	M332	Studies on the dependence of R_F values on the migration time, pH and concentration of the mobile phase, quantitative determination of separated metal ions by atomic absorption spectroscopy	477
Forty-nine inorganic ions	S167	M333		478
Ce^{2+}, Ce^{4+}, Nd, Eu, Gd, Tb, Yb, Y, Ti, V, Zr, Th	S170	M334	The R_F values of the lanthanide ions increase with increasing concen trations of citric acid in the mobile phase	479
Alkali metals	S171	M335	Qualitative separations	480

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Rare-earth elements	S172	M336	Qualitative separations	482
Cu, Co, Cd, Hg, Ni, Ag	S160, S95	M337	Qualitative separations and determination of chromatographic parameters as a function of the concentrations of MeOH, NH_3, AcOH, and inorganic salts in the mobile phase	483
V, Mn, Ag, Hg, Co, Ni, Cu, Zn, Pd, Cd, Hg, Cr, Fe, Ru, Rh, La, Au, Tl, Zr, Pt, Nb, Ta, Mo, W	S14, S173	M338	Run 11 cm; correlation between R_F values on impregnated layers developed with DMSO - THF (1 + 10) and the atomic numbers of the metal ions	484
Transition metal ions	S160, S95	M339	-	485
Twenty-one inorganic cations	S17	M340	Separation and identification of cations on cellulose layers using six detection reagents	486
Fe, Cu, Mn	S17	M341	Qualitative separations	487
Pb, Cd, Zn	S98	-	Application of TLC - square-wave anodic stripping voltametry for the determination of heavy metals	488
Mn, Co, Ni, Cu, Zn, Fe, Cr, Ti, V	S165	M342	Reversed-phase TLC for qualitative identification of 3d metal ions	489
Eleven metal ions	S174	-	Retention behavior of metal ions from aqueous solutions at pH 1–7 on impregnated silica layers	490
Fe, Co, Zn, Cd, Cu, Ni	S175	-	Application to the analysis of alloys and natural water samples	491
Metal ions	S176	M343	Qualitative separations	492
Mg, Al, Ca, V, Cu, Zn, Ge, Y, Zr, Mo, Ag, Cd, In, La, Ce, Eu, Tb, Tl, Pb, Bi	S177	M344	Detection limits and R_F values of fluorescent cations separated on porous glass sheet	493
Forty-nine inorganic ions	S178	M345	Separation of Sc(III), rare-earths (III), Y(III), Th(IV), and V(VI) from other ions	494
Cd	S179	M53	Study of the influence of soil properties and constituents on the mobility of cadmium by soil TLC	495
Rare elements	S164	M346	Preconcentration of rare-earths by circular TLC for subsequent ICP-AES determination in geological samples	496
Toxic metal ions	S5, S146 S199	M347	Normal and reversed phase and chelation TLC of some toxic metal ions; quantitative separation of Pb from binary mixtures and synthetic alloys	458
Hg, Ni, Cu, Co, Cd, Hg	S160	M348	Separation of mixtures of inorganic ions	497
Forty-nine inorganic ions	S180	M349	R_F value increases with increasing acid or sulfate in the mobile phase	498
3d Series transition metal ions	S181	M350	Examination of the effect of the concentration of H_2MEHP and HNO_3 on R_F values	499
Twenty-six transition and alkali metal ions	S17	M351	Qualitative separations	500
Uranium	S182	M352	Ascending technique; selective separation of uranium from synthetic mixture of several metal ions	501
Cations with some anions	S163	M353	TLC of cations and anions; qualitative separations	497
Inorganic ions	S184	M354	Separation of polyvalent ions and trivalent rare earths which tend to form anionic sulfate complexes	502

Table 3 (continued)

Cation/metal	Stat. phase	Mobile phase	Comment	Ref.
Inorganic metal ions	S200	M355	The effect of impregnants and of mobile phases of different pH on the mobility of inorganic ions	503
Copper	S14	M356	Layer thickness 0.25 mm; plate activation at 110°C; isolation of copper from biological tissue by dry oxidation and ashing; then chromatography on silica	504

[a]The stationary and mobile phases used are listed in Tables 4 and 5, respectively. A list of abbreviations is given in Table 6.

stationary and mobile phases used. The stationary and mobile phases are tabulated separately (**Tables 4** and **5**, respectively). A list of abbreviations is given in **Table 6**. The *relative proportions of publications on the analysis of these* groups are compared in **Figure 1**; the increasing interest in metal and metal ion analysis is reflected in the shape of the curve (curve I) for publications on these species. The growth in the TLC of metal ions slowed during 1981–82 when metal complexes became the choice of investigators. A decline in the number of publications on metal complex-

Table 4

The stationary phases used.

S1	Aluminum oxide [Macherey-Nagel (MN) Polygram Alox N]
S2	Alumina containing 5% gypsum
S3	Silufol
S4	DEAE cellulose in the formate form (Serva), microcrystalline cellulose
S5	Silica gel
S6	Commercial aluminum foil-backed silica gel
S7	Silica gel G_{254}
S8	*Sephadex G-25*
S9	Baker-flex DEAE cellulose, PEI-F cellulose, Kodak silica gel, and Baker-flex silica gel sheets
S10	Alumina
S11	Cellulose (MN-300) impregnated with polyethyleneimine
S12	Silica gel (Wakogel B-0)
S13	Silica gel with starch binder and fluorescent indicator
S14	Silica gel G
S15	Silica gel sheets
S16	Sephadex (G-200)
S17	Cellulose
S18	Cellulose (Merck plates; #5716)
S19	Microcrystalline cellulose
S20	Microcrystalline cellulose containing fluorescent indicator
S21	Silica gel KSS-4 calcined at 500°C for 6 h
S22	Silica gel H60
S23	Precoated cellulose plates (Merck)
S24	Hydrated stannic oxide
S25	Silufol 254
S26	Silica gel D
S27	Silica gel G + silpearl (1:1)
S28	Alumina G

Table 4 (continued)

S29	Silica gel H
S30	Silica gel impregnated with fluorescein
S31	Zirconium(IV) molybdate
S32	Polyamide
S33	Antimonic?? acid
S34	Silica gel impregnated with copper sulfate solution
S35	Alumina - silica gel G, 1:1, 1:2, 2:1
S36	Anhydrous antimony(V) oxide
S37	Silica gel impregnated with a 0.1%?? aqueous solution of $CuSO_4$, $ZnSO_4$, $NiCl_2$, $CoCl_2$, $Co(NH_3)_6Cl$
S38	Silica gel D (VEB Chemie-Werk, FRG) activated at 110°C for 30 min
S39	Cellulose, water, d-quartz and Na, K-tartrate blended in the ratio 40 g : 218 mL : 10 g : 5 g
S40	Silica gel (Wakogel B-5)
S41	Commercial silufol plates (Kavalier, CSSR)
S42	Silica gel KSK
S43	Silica gel Woelm
S44	Silica gel G (MN Polygram)
S45	Silica gel (Merck, Darmstadt)
S46	Silica SHR MN Polygram
S47	Silica gel - starch, 19:1
S48	Styragel 60A (polystyrene - divinylbenzene copolymers)
S49	Cellulose (MN-300)
S50	Aluminum foil-backed plates
S51	Merckogel OR-PVA 2000
S52	Silica gel 60 (without fluorescent indicator), silica gel 60 F_{254}, silanized silica gel 60 F_{254}
S53	Sephadex LH-20
S54	Sephadex G-10
S55	Sephadex G-15
S56	Silica gel G - starch, 24:1 *w/w*
S57	Alumina with plaster of Paris binder
S58	Silica gel G - starch, 95:5 *w/w*
S59	Silica
S60	Polyacrylonitrile
S61	Silufol sheets (aluminum-backed silica gel)
S62	Silica gel (kieselgel 60G, Merck, Darmstadt, FRG) on microscope slides
S63	Octylsilanized silica gel F_{254} HPTLC plates
S64	Silica gel impregnated with chlorobenzene
S65	Silica gel containing NaOAc or NH_4OAc
S66	Silica gel, silica gel 60 F_{254} and 60 F_{2545} HPTLC plates

Table 4 (continued)

S67	Silica gel G and precoated RP-18 plates
S68	Silica gel impregnated with different surfactants
S69	Silica gel G-HR??
S70	Microcrystalline cellulose LK??
S71	Cellulose powder (Whatman CC41, mean particle size 0.25 mm)
S72	Sodium carboxymethyl cellulose and Dowex 50 3 4 (Na^+ form)
S73	Silica gel KSK - NH_4NO_3 as salting out agent - starch (1:0.1:0.01)
S74	*MN cellulose 300 Avicel (R) - cellulose, 1:1* equilibrium mixture
S75	DEAE cellulose in the phosphate form
S76	Modified chelate - formic cellulose containing azorhodamine, groups and azorhodamine
S77	Microcrystalline cellulose LT + LiCl and cellulose DEAE
S78	DEAE cellulose in the sulfate form
S79	Silica gel HR - starch, 135:2
S80	Diatomite treated with acid
S81	Ecteola - cellulose in the chloride form
S82	Stannic arsenate
S83	*Silica gel (Silufol, Kavalier, CSSR) saturated with* 4 M $LiNO_3$
S84	Stannic antimonate
S85	Silica gel impregnated with L-ascorbic acid
S86	Silica gel impregnated with EDTA
S87	Cellulose phosphate in the H^+ form
S88	Silanized silica gel (Merck, Darmstadt) and polygram plate
S89	Stannic tungstate in the H^+ form
S90	Cellulose powder and cellulose impregnated with Bu_3PO_4 in CCl_4
S91	Silica gel impregnated with *p*-toluidine
S92	*b*-Stannic arsenate
S93	Silica gel impregnated with pyridinium tungstoarsenate
S94	DEAE cellulose in the chloride form
S95	Chitosan
S96	Silica gel G impregnated with nitriloacetic acid
S97	Dowex w-x8 cation exchanger - silica gel, 1:1, and Amberlite IRA??-400 anion exchanger - silica gel mixtures
S98	Carboxymethylcellulose
S99	Silica gel impregnated with diethylenetriamine
S100	Silica gel G impregnated with DCTA
S101	Silica gel G - La tungstate gel
S102	DEAE cellulose
S103	Microcrystalline cellulose with solutions containing pyrocatechol violet
S104	Sulfoethyl cellulose (strongly acidic) cation exchanger
S105	Th(IV) antimonate
S106	Thorium tungstate (binder-free)
S107	Silica gel and cellulose impregnated with different concentrations of hydrochloric acid
S108	silica gel impregnated with ceric molybdate
S109	Precoated plates; Fixion 50x8 (H+ or Na+) saturated with *mobile phase vapors*
S110	Cellulose phosphate (Whatman P41, UK) and cellulose phosphate + microcrystalline cellulose (3:1)
S111	Zr tungstate
S112	MN cellulose 300G containing 10% $CaSO_4$
S113	Lanthanum antimonate (binder-free)
S114	Silica gel and vionit CS-32 ion-exchange resin

Table 4 (continued)

S115	Ecteola - cellulose
S116	Dowex 1 or 50 mixed with plain cellulose (Avicel SF)
S117	Silica gel and Dowex 50x8 cation-exchange resin
S118	Sulfoethyl cellulose (Serva, Heidelberg, FRG)
S119	Ti(IV) antimonate in the H^+ form
S120	Glass powder
S121	Corn starch
S122	Mixture of silica gel, starch, and NH_4NO_3
S123	Silica gel impregnated with 0.5% sulfaguanidine
S124	Silica gel impregnated with 8-hydroxyquinoline and dibenzoylmethane
S125	Silica gel R and 15% vionit CS ion exchanger
S126	Silica gel impregnated with aqueous sodium molybdate
S127	Silica gel impregnated with organophosphorus compounds
S128	Cellulose phosphate in the H^+ form (Whatman P41, UK)
S129	Silica gel impregnated with 0.5% aqueous 2,2-dipyridyl and iminodiacetic acid
S130	Hydrous zirconium oxide
S131	Silica gel impregnated with 30% *s*- or *t*-butylamine
S132	*Silica gel impregnated with crystalline antimonic(V) acid - p*-sulfochlorophosphonazo
S133	Tin(IV) arsenosilicate and arsenophosphate
S134	Semicrystalline Sn phosphate ion exchanger silica gel G
S135	Silica gel 60
S136	PEI cellulose
S137	Silica gel G mixed with chitosan
S138	Cellulose with azopyrocatechol group
S139	Silica gel impregnated with 0.5 M NH_4Cl and a saturated aqueous solution of $Ba(NO_3)_2$
S140	Silica gel - NH_4NO_3 - CM-cellulose, 5.0:0.64:0.16 *w/w*
S141	Tin pyrophosphate and silica gel containing sodium carboxymethylcellulose as binder
S142	Silica gel - sodium carboxymethylcellulose - NH_4NO_3
S143	Silica gel - NH_4NO_3 - sodium carboxymethylcellulose - H_2O, 33:4:1:100 *w/w*
S144	Silica gel impregnated with hydroxybenzoic acid
S145	Silica gel impregnated with 0.1 M aqueous $NaNO_2$, sodium molybdate, and potassium dihydrogen orthophosphate
S146	Silica gel loaded with various concentrations of tributylamine
S147	*Silica gel - starch - ammonium rhodanate,* 2.8:0.15:0.5 *w/w*
S148	C_{18}-bonded silica reversed phase layer
S149	C_{18}-bonded silica
S150	Binder free Zr(IV) antimonate in the H^+ form, silica gel G, and a 1:1 mixture of Zr(IV) antimonate and silica gel G
S151	Silica gel H - microcrystalline cellulose - NH_4NO_3
S152	Silica gel impregnated with sodium molybdate
S153	Silica gel impregnated with 0.1–1.0 M aqueous solutions of NaCl, NH_4Cl, KBr, or KI
S154	Silica gel treated with acid
S155	Stannic silicate
S156	Silica gel H and sodium carboxymethylcellulose
S157	Silufol UV_{254} impregnated with 5% paraffin oil in hexane
S158	Microcrystalline cellulose modified with silica gel G
S159	Polychrom (porous polymer, particle size 10–40 mm) in combination with polyvinyl alcohol

Table 4 (continued)

S160	Chitin
S161	Natural silt loam and clay loam soils, autoclaved soil, natural soil, natural soil modified with 5% $CaCO_3$, soil mixed with 5% fly ash, soil treated with Ca^+, H^+, or Na^+, soil treated with 1% $CaSO_4$, $MgSO_4$, $NaHCO_3$, Na_2CO_3, or Na_2SO_4 solutions
S162	Zirconium phosphoantimonate
S163	Silica gel impregnated with different concentrations of mono-2-ethylhexyl acid phosphate (H_2MEHP)
S164	Fixion 50 3 8
S165	Silica gel coated with high molecular weight amines (Primine JM-T, Amberlite LA-1, Alumine 36, Aliquat 336)
S166	Silica gel impregnated with salicylic, syringic, or *o*-phthalic acids
S167	*p*-Aminobenzylcellulose
S168	Diethyl-(2-hydroxypropyl)aminoethyl Q E-cellulose (strong basic anion exchanger)
S169	Synthesized carbamide - formaldehyde polymer (*Aminoplast*)
S170	Silica gel coated with different concentrations of Primine JM-T
S171	Zinc ferrocyanide
S172	Diatomite
S173	Silica gel impregnated with DMSO
S174	Silica gel impregnated with a mixture of alizarin red S and Aliquat 336
S175	Silica gel modified with an analog of dibenzo-18-crown-6
S176	Mixtures of silica and inorganic ion-exchange gels
S177	Porous glass sheets
S178	*Diethyl-(2-hydroxypropyl)aminoethylcellulose*
S179	Twenty-two soils with different characteristics
S180	Silica gel impregnated with high molecular weight amines
S181	Silica gel impregnated with mono-2-ethylhexyl acid phosphate (H-MEHP)
S182	Stannic sulfosalicylate
S183	Mixed adsorbent layers
S184	Trimethyl hydroxypropylamine cellulose (QA)
S185	Silica gel (with and without gypsum binder)
S186	Silicon dioxide prepared from tetraethoxysilicon by alkaline liquid-phase hydrolysis, and thermochemical SiO_2 prepared from tetraethoxysilicon under different conditions of alkaline hydrolysis, drying, and calcination
S187	Microcrystalline cellulose Avicel RSF
S188	Commercial aluminum-backed cellulose plates
S189	Triethylaminoethylcellulose
S190	Polygram silica plates
S191	Mixtures of alumina and silica in different ratios
S192	Cellulose impregnated with EDTA
S193	Semicrystalline stannic arsenate
S194	Layers impregnated with nitriloacetic acid
S195	Silica gel impregnated with nitriloacetic acid
S196	Dowex 50x8 cation-exchange resin
S197	Silica gel with hydrous manganese dioxide
S198	Silica gel H - NH_4NO_3 - CM-cellulose, 5 0 0 64 0 16 *w/w*
S199	Silica gel impregnated with tributylphosphate
S200	Surface-modified sorbent layers
S201	Silica gel impregnated with tri-*n*-octylamine

Table 5

The mobile phases used.

M1	Aqueous solutions of KNO_3, Na_2CO_3, NaOAc, HOAc, K_2SO_4, K_3PO_4, NaF, acids and bases, and buffer solutions
M2	Methanol or water - 28% ammonia (10 + 1)
M3	Ethanol - dioxane - water - aqueous ammonia (6 + 12 + 10 + 5)
M4	Aqueous formic acid solutions
M5	Acetone, dioxane mixed with NaOH or aqueous ammonia
M6	Acetone - formic acid - water (7 + 1 + 1), butanol - ethanol - water (1 + 3 + 1), distilled water, propanol - $CHCl_3$ - benzylamine (6 + 3 + 1)
M7	0 1 M KNO_3
M8	0 01 M HCl, 4 M LiCl, ethanol - 0 01 M HCl (1 + 1)
M9	NH_4NO_3 (3–6 M), ammonium hexafluorophosphate (3 M), acetone - heptane - aqueous tetrabutylammonium chloride (12 + 2 + 0 5, 9 + 3 + 0 5)
M10	Water and 0 1–1 N NaOH
M11	2 M LiCl
M12	Several mixed solvent systems consisting of dioxane, methanol, ethanol, butanol, octanol, propanol, aqueous ammonia and ammonium acetate
M13	Acetone - butanol - 25% aqueous NH_3 - water (13 + 4 + 2 + 1)
M14	Ethanol - pyridine - water - aqueous ammonia (12 + 5 + 4 + 1)
M15	Acetone, acetone - water (83 + 17)
M16	0 01 N HNO_3, 3 N $LiNO_3$, 3 N CH_3COOLi, and 0 01 N HNO_3 - ethanol (1 + 1)
M17	water, aqueous ammonia, single-component organic solvents and multicomponent aqueous organic solvents
M18	*28% aqueous ammonia - acetone - n-butanol* (6 + 13 + 3), 28% aqueous ammonia - acetone (2 + 3), dioxane - water (3 + 2), acetone - acetic acid - water (20 + 1 + 20)
M19	Twenty-six mixed aqueous organic solvent systems containing acetone, methanol, ethanol, butanol, propanol, dioxane, ether, acetylacetone, ethylene??, glycerol or ammonia
M20	Binary, ternary, quaternary, and penternary mixtures of aqueous and organic solvents containing water, ammonia, acetone, methanol, ethanol, butanol, *n*-propanol, pyridine, or ether
M21	Twenty-seven mobile phases of various compositions
M22	Basic and polar solvent systems
M23	Acetone - benzene - water (16 + 5 + 2)
M24	Ethanol - water (7 + 4), butanol - C_5H_6N - water - 25% aqueous ammonia (16 + 8 + 16 + 1)
M25	28% aqueous ammonia - acetone - *n*-butanol (6 + 13 + 3)
M26	Acetone - formic acid - water (7 + 1 + 1)
M27	Various alcohols mixed with aqueous ammonia
M28	Various alcohols mixed with aqueous ammonia
M29	Buffered aqueous ammonia (pH 10)
M30	Concentrated aqueous ammonia - *n*-propanol (1 + 2), pyridine - water - *n*-butanol (3 + 3 + 5)
M31	Methanol - benzene - ethyl acetate - ethyl methyl ketone - aqueous ammonia (6 + 6 + 6 + 2 + 1)
M32	Acetone - benzene (1 + 1)
M33	Butanol - acetone - water (9 + 9 + 2)
M34	Acetone - water (10 + 1), methanol - water - butanol (3 + 1 + 1), butanol saturated with 2 N HNO_3
M35	Butanol - propanol - water (1 + 3 + 1)

Table 5 (continued)

M36	Many single-component and mixed solvent systems containing 36 polyhydric alcohols, methylamine, aqueous ammonia, dimethylformamide, water, ketones, pyridine and esters.
M37	Acetone - butanol - 10% aqueous ammonia - water (13 + 4 + 2 + 1)
M38	Propanol - aqueous ammonia (2 + 1)
M39	Tetrahydrofuran - acetic acid - water (10 + 1 + 1)
M40	Acidic solvent systems
M41	Acetone - *n*-butanol - conc. aqueous ammonia - water (3 + 4 + 2 + 1), and *n*-butanol - ethanol - conc. aqueous ammonia - water (2 + 2 + 1 + 1)
M42	20% acetic acid - dioxane - 88% isopropanol - 9% trichloroacetic acid - methanol (1 + 2 + 3 + 5 + 10)
M43	Pyridine - water - *n*-butanol - aqueous ammonia (4 + 8 + 92 + 1)
M44	Toluene - acetic acid (5 + 2)
M45	Butanol - formic acid (1 + 1)
M46	Methanol - water - trichloroacetic acid - butanol or propanol (7 + 5 + 1 + 7)
M47	Isopropanol - 13.5% trichloroacetic acid - 25% aqueous ammonia (140 + 40 + 0.6)
M48	Aqueous organic acids
M49	Aqueous sodium salicylate
M50	Sixty-nine organic solvent systems (single-component, two-component, and three component systems comprising amine alcohols, ketones, or phenols and formic acid)
M51	Water - ethanol - 2-methylpropanol - 2-propanol - aqueous ammonia - trichloroacetic acid (150 + 175 + 75 + 107 + 2 + 25)
M52	Acetone mixed with 0.1 M aqueous HCl, NaCl, HBr, formic acid, or aqueous ammonia (1 + 9 or 9 + 1)
M53	Distilled water
M56	Mixed acidic - organic solvent systems containing formic acid
M55	Acetone - DMSO or formic acid, acetone - DMSO - formic, and acetone - mineral acid mixtures
M56	Acetone - chloroform (3 + 1)
M57	Dichloromethane - petroleum ether (5 + 3)
M58	$CHCl_3$ - *n*-hexane (3 + 7)
M59	Aqueous mixture of sodium or potassium D-tartrate and/or $AlCl_3$
M60	Monocomponent and bicomponent solvent systems containing methanol, ethanol, cyclohexanol, acetone, methyl ethyl ketone, ethyl acetate, diethyl ether, CCl_4, $CHCl_3$, ethylene chloride, CS_2, *n*-hexane, cyclohexane, benzene, xylene, nitrobenzene, *o*-dichlorobenzene, and benzonitrile
M61	0.1, 1.0 and 6.0 N H_2SO_4, 0.2 or 0.5 M tetraoctylamine in benzene
M62	Aqueous solutions of various inorganic salts and acids
M63	CCl_4, toluene, benzene, dichloromethane, diethyl ether
M64	Benzene - ethanol - 25 aqueous ammonia
M65	Dry cyclohexane
M66	CH_3COOH - $CHCl_3$ (1 + 99, 1 + 49, 12 + 48), light petroleum - toluene (67 + 33), CH_3COOH - water - toluene (7 + 3 + 10, 17 + 3 + 20), CH_3COOH - water - light petroleum (17 + 3 + 20, 9 + 1 + 10), upper phases of CH_3COOH - water - light petroleum - toluene (85 + 15 + 50 + 50, 85 + 15 + 67 + 33), and CH_3COOH - water - light petroleum - toluene - methanol (95 + 15 + 67 + 33 + 1)

Table 5 (continued)

M67	Acetonitrile, dioxane, acetone, methanol, ethanol, butanol, acetic acid, BuOH - HOAc (4 + 1, 3 + 2, 2 + 3, 1 + 4), HOAc - water (1 + 4)
M68	CCl_4 - $CHCl_3$ (10 + 1), toluene - benzene (10 + 1)
M69	$CHCl_3$ - acetone (5 + 2), $CHCl_3$ - methyl isobutyl ketone - benzene (4 + 2 + 1)
M70	Hexane - diethyl ether or acetone (9 + 1), hexane - acetone (4 + 1)
M71	~~dichloromethane~~ methylene chloride - methanol (9 + 1), benzene
M72	(a) Mixtures of chloroform and benzene, ethyl acetate, pyridine, acetone, or methanol (9 + 1) (b) Mixtures of CS_2 and benzene, hexane, chloroform, or CCl_4 (1 + 1)
M73	Acetonitrile, methanol, ethanol, butanol, acetic acid, or butanol - acetic acid (4 + 1, 3 + 2, 2 + 3, 1 + 4)
M74	Acetonitrile, dioxane, acetone, methanol, ethanol, butanol, acetic acid, or butanol - acetic acid (4 + 1, 3 + 2, 2 + 3, 1 + 4).
M75	Dioxane
M76	Methyl ethyl ketone, methanol - water (17 + 3), 0.3 N HCl
M77	Mono- and two-component organic solvent systems
M78	CCl_4 - benzene - ethylene dichloride (1 + 2 + 2)
M79	Ethanol - benzene or toluene (1 + 1 to 1 + 4), methanol - benzene or toluene (1 + 1, 1 + 4)
M80	$CHCl_3$, *p*-dioxane, benzene, 10^{-3}-10^{-1} M HOx in $CHCl_3$, 10^{-2} M HOx in *p*-dioxane, 10^{-1} M pyridine in $CHCl_3$
M81	Several organic, mixed organic and mixed aqueous - organic solvent systems
M82	Methanol, dioxane, nitrobenzene - methanol (1 + 4), benzene - acetone (1 + 4)
M83	CH_2Cl_2 - tetrahydrofuran (9 + 1, *v/v*), CH_2Cl_2, $CHCl_3$
M84	Mixed organic solvent systems containing benzene
M85	Water, 10^{-2} M HCl, and various concentrations of NaCl solutions
M86	CCl_4, 1,1,1-trichloroethane
M87	Methanol, ethanol, butanol, AcOH, butanol - AcOH (1 + 1, 1 + 2, 2 + 1), aq. butanol - AcOH - $CHCl_3$ (5 + 5 + 1, 5 + 5 + 2, 5 + 5 + 3), butanol - hexane - $CHCl_3$ (1 + 2 + 1, 2 + 1 + 1)
M88	Distilled water, MeOH, EtOH, ethylene glycol, monomethyl ether, dimethylsulfoxide, *N,N*-dimethylformamide, acetonitrile, 1,2-propanediol, and 1,3-propanediol
M89	Different solvent mixtures
M90	*Iso*-BuOH - MeOH - CCl_4 - O.15 M NaCl (9 + 6 + 4 + 1)
M91	Solvents of moderate polarity (dichloromethane and benzene)
M92	*n*-butanol - benzene (1 + 1, *v/v*), *n*-butanol and acetic acid
M93	Acetone, *n*-butanol - benzene
M94	Highly polar amines
M95	CH_2Cl_2 , $CHCl_3$, CCl_4, C_6H_6, butanol, C_6I_6 - butanol (1 + 1, 2 + 1, 1 + 2)
M96	Acetone
M97	$CHCl_3$ and *i*-Pr_2O
M98	Single-component and multicomponent organic and aqueous - organic solvent systems
M99	Water, 0.01 M HCl, aqueous NaCl (0.01, 0.1 M)
M100	EtOAc media
M101	Mixture of Me_2CO and $CHCl_3$
M102	Acidic solutions containing 0.05–2.0 mL H_2SO_4 L^{-1}

Table 5 (continued)

M305	Demineralized water, 0 1 M formic acid, 1 0 M KI, KBr, or NaCl, 0 1 M formic acid - 0 1 M KI or KBr (1 + 9), 1 0 M formic acid - 1 0 M HBr (1 + 9 and 9 + 1), 1 0 M formic acid - 1 0 M NaCl, NH_4Cl, KBr, or KI (1 + 9, 3 + 7, 1 + 1, 7 + 3, and 9 + 1)
M306	Ethyl acetate - acetone (8 + 7) - formic acid - water (4 + 1)(8+7)
M307	Thirty-six solvent systems
M308	0 2 M acetic acid - 0 2 M sodium acetate systems
M309	Organic solvent mixtures consisting of Di-(2-ethylhexyl) phosphate, mono-(2-ethylhexyl) phosphonate, tributyl phosphate, tetrahydrofuran, nitric acid, and isopropyl ether in different ratios
M310	10% ammonium acetate with aqueous ammonia
M311	*n*-Butanol - methyl isobutyl ketone - p20 - HCl (140 + 100 + 15 + 18) and (140 + 100 + 15 + 1)
M312	Mixtures of ethanol and aqueous NaCl or HCl
M313	Aqueous - methanolic solutions (1 + 1 3 + 1, *v/v*) of ammonia or acetic acid with ammonium nitrate, or sometimes ammonium acetate
M314	Aqueous solutions of sodium malonate and sodium malate
M315	Distilled water and buffer solutions (pH 5 2, 7 2, or 9 2)
M316	0 05 M glycolic acid at pH 2 5 (adjusted with HCl)
M317	Aqueous solutions of HCl, HBr, H_2SO_4, HNO_3, H_3PO_4 and various organic acids
M318	MeOH - EtOH - NH_4Cl - aqueous ammonia
M319	Buffered EDTA solutions
M320	HNO_3 (0 05–3 0 M)
M321	Mixed H_2SO_4 and dioxane systems
M322	Oxalic acid and NH_4Cl solutions
M323	Aqueous solutions of organic and inorganic acids
M324	Aqueous solutions of alkali-metal chlorides
M325	Mixtures of 2 5 M HCl, 2 5 M NaCl, and 0 6% hydrogen peroxide in different ratios
M326	0 03 M citric acid
M327	Distilled and tap water
M328	H_2SO_4 (0 01–1 0 M) and H_2SO_4 - ammonium sulfate (0 01–1 0 M) systems
M329	Aqueous hydrochloric acid and HCl - ammonium chloride (0 01–1 0 M) systems
M330	HNO_3 - HCl or H_2SO_4 containing different concentrations of hydrogen peroxide
M331	Eleven neutral and acidic solvent systems
M332	Aqueous solutions of sodium thioglycolate (0 01–0 2 M)
M333	Aqueous HCl and aqueous HCl - ammonium chloride mixtures
M334	0 01–1 0 M citric acid
M335	Aqueous ammonium nitrate
M336	Solutions of acids, bases, and salts
M337	1 M inorganic salt solutions in aqueous methanol
M338	DMSO - 1 0 M HNO_3 (1 + 1), DMSO - THF (1 + 10), *n* butanol - acetone - HNO_3 (6 + 6 + 1), diisopropyl ether - DMSO (10 + 1), and DMSO - THF - diisopropyl ether systems
M339	Several aqueous mobile phases
M340	Acetylacetone - acetone - conc HCl (5 + 5 + 1)
M341	Ethanol - isobutanol - conc HCl - water (12 + 6 + 1 + 1)
M342	0 001–0 1 M aqueous solutions of succinic acid
M343	Sixteen different solvent systems
M344	*n*-Butanol - benzene - 1 M HNO_3 - 1 M HCl (75 + 69 + 4 + 2, *v/v*) or acetone - 3 M HCl (99 + 1, *v/v*)

Table 5 (continued)

M345	Aqueous sulfuric acid and sulfuric acid - ammonium sulfate media
M346	0 1 M $H_2C_2O_4$, 2 M NH_4Cl, 5 M HCl, 0 5 M ammonium citrate
M347	DMSO - HNO_3 and DMSO - HCl systems
M348	Buffer solutions
M349	Sulfuric acid, sulfuric acid - ammonium sulfate mixture
M350	HNO_3 at different concentrations
M351	Four mobile phases
M352	Mixtures of dimethylformamide and nitric or hydrochloric acid
M353	Aqueous MeOH containing tributyl phosphate and formic acid
M354	Sulfuric acid and organic solvents
M355	Formic acid and sodium formate
M356	MeOH - AcOH (100 + 0 3, *v/v*)
M357	Chloroform, benzene, or ACOEt - CCl_4 (1 + 4), MeCN - CCl_4 (1 + 4)

Table 6

List of abbreviations used in Tables 1–5. (Metals are in their usual valence state unless otherwise stated.)

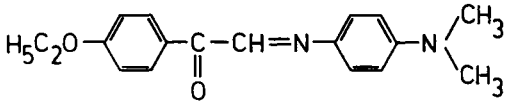
A	*p*-Dimethylaminoanil of 3-benzoylmethylglyoxal
acac	2,4-Pentanedionation is acetylacetonato ion
ala	Alanine
B	*p*-Diethylaminoanil of 3-benzoylmethylglyoxal
bpy	Bipyridine
bzac	1-Phenyl-1,3-butanedione ion
CTAB	*N*-cetyl-*N,N,N*-trimethylammonium bromide
DEDTC	Diethyldithiocarbamate
dip	Dipylcidal
en	Ethylenediamine
gly	Glycine
H_2MEHP	Mono-2-ethylhexyl acid phosphate
Hox	Hydroxyquinoline
L	
Leu	Leucine
ophen	*o*-Phenanthroline
Ox	Oxyquinoline
PC	Paper chromatography
phen	Phenanthroline
phac-phac	1,3-Diphenyl-1,3-preponedionatoion?? is dibenzoylmethanato ion
REE	Rare-earth elements
SDBM	3-Mercapto-1,3-diphenyl-2-propen-1-one
SDS	Sodium dodecyl sulfate
STTA	1,1,1-Trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one
TGBA	Thiophene-2-glyoxal-*p*-bromoanil
TGDEA	Thiophene-2-glyoxal-*p*-diethylaminoanil
TGDMA	Thiophene-2-glyoxal-*p*-dimethylaminoanil
TPP	Tetraphenylporphyrin complexes
val	Valine

Table 5 (continued)

M247	Isoamyl alcohol - water - AcOH (2 + 1 + 1), methanol - benzene - AcOH (4 + 2 + 3)
M248	Aqueous solutions of inorganic acids ($HClO_4$, HCl, HBr, HNO_3, H_2SO_4, and H_3PO_4), their mixtures, and some of their salts
M249	Aqueous HCl and HNO_3 of different pH and their mixtures with organic solvents in different ratios
M250	1.0 M HCOOH, 1.0 M HCOONa, and their binary mixtures (1 + 1, 2 + 8, 4 + 6, 6 + 4, 8 + 2)
M251	Aliphatic alcohol - HCl systems
M252	Isopropyl ether - THF - tributyl phosphate - HNO_3 (10 + 6 + 1 + 1)
M253	*iso*-PrOH - Et_2O - EtOAc - HNO_3 (20 + 20 + 10 + 1), *iso*-PrOH - THF - HNO_3 (30 + 10 + 1)
M254	Potassium pyrophosphate solution
M255	Buffered EDTA solution
M256	Mixture of organic solvents
M257	20.0 M formic acid in butanol
M259	Ammonium nitrate solutions of different concentrations (0.5–6.0 M) with constant pH (4.9 + 0.1)
M259	Ethanol - HCl (4 + 1, 9 + 1); ethanol - HNO_3 (9 + 1), isopropanol - HCl (9 + 1), and ternary mixtures of organic, aqueous, and mineral acids in different ratios
M260	0.01–1.0 M HCl
M261	*n*-Butanol - hydrochloric acid (2 + 1, 3 + 1, 4 + 1, 9 + 1, 17 + 3); the best solvent for the separation of a cation mixture is *n*-butanol - conc. HCl (17 + 3)
M262	Aqueous solutions of HCl (0.1–0.5 M), buffer solutions of different pH, aqueous - organic mixtures of different composition
M263	Aqueous solutions of HCOOH, HCOONa, CH_3COOH, CH_3COONa, acetic acid - sodium acetate (1 + 1), and formic acid - sodium formate (1 + 1)
M264	Aqueous formic acid solutions containing DMSO, acetone, or ethyl methyl ketone; methyl isobutyl ketone saturated with formic acid; aqueous formic acid
M265	Aqueous H_2SO_4 (0.01–0.1 M) and sulfuric acid - ammonium sulfate (0.01–1.0 M solutions)
M266	Phosphate - Et_2O - HNO_3 (40 + 40 + 0.8, 20 + 42 + 2.5)
M267	P_{204} - dioxane - EtOAc - HNO_3 (1 + 1 + 2, 0 + 2.4 + 4)
M268	Tributylphosphate - THF - diethyl ether - HNO_3 (1 + 9 + 9 + 1.5)
M269	Eleven organic mobile phases consisting of hydrocarbons and their derivatives in different ratios
M270	0.05–2.0 M formic acid in butanol
M271	Mixtures of 0.05 M HCl and 0.01–1.0 M ammonium thiocyanate in different ratios
M272	Acids (nitric, tartaric, citric, perchloric, formic), bases (aqueous ammonia, trimethylamine), neutral compounds (NH_4Cl, NH_4NO_3, $AcONH_4$ or mixtures of these with organic solvents (EtOH, MeOH, *n*-PrOH, Me_2CO)
M273	Monotetradecylphosphoric acid(I??) - diethyl ether - conc. HNO_3, 2.0 + 42 + 2.5 (solvent A) and 4.0 + 40 + 0.8 (solvent B)
M274	Et_2O - THF - bis(2-ethylhexyl)phosphate - HNO_3
M275	P_{507} - methyl isobutyl ketone - *iso*-Pr_2O - HNO_3 (1 + 12 + 6 + 2.4 *v/v*)
M276	*n*-propyl alcohol - ethyl acetate - conc. HNO_3 (10 + 30 + 1), *n*-propyl alcohol - dichloromethane - conc. HNO_3 (10 + 30 + 1, 30 + 10 + 1), *n*-propyl alcohol - cyclohexane - anhydrous alcohol - conc. HNO_3 (20 + 15 + 15 + 1), *n*-propyl alcohol - petroleum ether - tetrahydrofuran - conc. HNO_3 (25 + 15 + 15 + 1)

Table 5 (continued)

M277	Mixed organic solvents containing *s*-butylamine
M278	10 M HCOOH in butanol - ethyl methyl ketone (1 + 1, 2 + 1, 1 + 3, 3 + 1)
M279	Aqueous HCOONa (10^{23}, 10^{22}, 0.1, 1.0, and 5.0 M), 0.1 M HCOONa - 0.1 M HCOOH (1 + 9, 3 + 7, 1 + 1, 7 + 3, and 9 + 1), 1.0 M HCOONa - 1.0 M NaCl (1 + 1, 1 + 2, 2 + 1, 1 + 9, and 9 + 1), mixture of 0.1 or 1.0 M HCOONa and 0.1 or 1.0 M NaCl, KBr, KI, or $KBrO_3$ in different ratios
M280	Mixtures of aqueous 1.0 M formic acid and alkaline salt solutions
M281	Ternary mixtures of different ratios of tributylamine, formic acid, and acetone
M282	Aqueous formic acid (10^{23}-20 M), aqueous sodium formate (10^{23}-5 M), and mixtures of 1.0 M formic acid and 1.0 M sodium formate (1 + 1, 4 + 6, 6 + 4, 2 + 8, and 8 + 2)
M283	Binary mixtures containing dimethylamine (DMA) and distilled water, methanol; or butanol; ternary mixtures containing DMA, acetone or ethyl acetate, and formic acid
M284	Trialkylmethylammonium chloride - *n*-octyl alcohol - petroleum ether - conc. HNO_3 (60 + 7 + 25 + 1)
M285	Tri-*n*-octylamine or tri-*iso*-octylamine - 4-methyl-2-pentanone - isopropyl ether - isopropyl alcohol - HNO_3 (1 + 8 + 8 + 6 + 0.75, *v/v*)
M286	Trimethylammonium chloride - *n*-octyl alcohol - petroleum ether - HCl (2 + 10 + 30 + 1, 2 + 6 + 30 + 1.2, and 2 + 7 + 30 + 1, *v/v*)
M287	P204 - P507 - tributyl phosphate - tetrahydrofuran - HNO_3 - diisopropyl ether (111 + 52 + 5 + 521 + 86 + 1000 and 68 + 43 + 27 + 460 + 103 + 1000, *v/v*)
M288	I. Bis(2-ethylhexyl) phosphate - diisopropyl ether - diethyl ether - nitric acid (1 + 10 + 6 + 1.1), II. Mono(2-ethylhexyl) phosphate - isopropyl ether - ethyl ether - nitric acid (1 + 8 + 8 + 1.1)
M289	Methanol - lactate media
M290	Mixed aqueous - hydroxyisobutyric acid solutions containing methanol
M291	Methanol - CH_2Cl_2 (1 + 99)
M292	HNO_3 (10^{24} - 1.0 M), DMSO - 0.1 M HNO_3 (1 + 0, 4 + 1, 3 + 2, 1 + 4), dioxane - 0.1 M HNO_3 (1 + 0, 4 + 1, 3 + 2, 2 + 3, 1 + 4)
M293	Aqueous alkali metal nitrate solutions
M294	Bis-(2-ethylhexyl) phosphate (P_{204}?? + 2-ethylhexyl(2-ethyl) phosphoric acid (P507??) - THF - HNO_3 - isopropyl ether, 3 + 2 + 90 + 19 + 280, 17 + 2 + 110 + 18 + 20, *v/v*).
M295	Mixed solvent systems consisting of mono(2-ethylhexyl phosphate, 4-methylpentanone, nitric acid, isopropyl ether, and/or tetrahydrofuran in different ratios
M296	*n*-Butanol - HCl - acetone (100 + 1 + 100)
M297	(I) P507 - mono(2-ethylhexyl) phosphonate - diethyl ether - conc. HNO_3 (1.5 + 43.5 + 2) and (II) P507 - diethyl ether - conc. HNO_3 (3 + 42 + 1)
M298	Formic acid - butanol systems
M299	Aqueous solutions (0.01–0.2 M) of acetic acid and chloro-substituted (mono-, di-, and trichloro) acetic acids
M300	Aqueous solutions of sodium acetate
M301	Mixed HCl - organic solvent systems (0.1 M HCl - ethanol or acetone (1 + 0.7, 3.1 + 1, and 3 + 7)
M302	Mixed H_2SO_4 - organic (methanol or acetone) solvent systems
M303	0.1 M HCl - dioxane (7 + 7, 5 + 5, 3 + 7, v/v)
M304	Isopropanol - tetrahydrofuran - 50% HNO_3 (60 + 20 + 3)

Table 5 (continued)

M103	Several solvent systems consisting of ketones, esters, alcohols and dioxane
M104	Single and binary solvent systems
M105	Organic solvents ## 106 Monocomponent organic solvents
M107	Methyl chloride, dioxane, acetic acid, methanol, ethanol, aq. butanol, butanol - AcOH (1 + 1, 1 + 2, 2 + 1), aq. butanol - $CHCl_3$ (5 + 1, 5 + 2), aq. butanol - AcOH - $CHCl_3$ (5 + 5 + 1, 5 + 5 + 2, 5 + 5 + 3)
M108	1% methanol in CH_2Cl_2
M109	Mixtures of water and alcohols
M110	Mixtures of xylene, absolute alcohol, and petroleum ether in different ratios
M111	PrOH - BuOH - water (4 + 3 + 3), EtOH - water (4 + 1)
M112	Twenty-two single-component solvents
M113	HCl solutions containing different amounts of ammonium thiocyanate and $SnCl_2$
M114	Water, aqueous solutions (0.1–1%) of $KClO_4$ and $HClO_4$
M115	Cyclohexane - acetone or methanol
M116	Two monocomponent and six polycomponent non - aqueous solvent systems
M117	Chloroform or toluene
M118	Organic solvent - mineral acid mixtures
M119	Mixture of water and dioxane or acetonitrile
M120	Aqueous solutions of KCl, K_2SO_4, $Na_2S_2O_3$ and KNa-$C_4H_4O_6$
M121	Distilled water, methanol, ethylene glycol, 1,2-propanediol, 1,3-propanediol
M122	Butanol - aqueous ammonia - water (15 + 3 + 5)
M123	Toluene
M124	*n*-Hexane, *n*-nonane, *n*-hexane - CCl_4 or benzene (9 + 1), water - acetone (1 + 4), water - tetrahydrofuran (THF) (3 + 7)
M125	Ethanol - butanol - water (20 + 60 + 47)
M126	*m*-Xylene
M127	Toluene - chloroform (50 + 1), benzene - methyl isopropyl ketone (50 + 1), methanol - water - acetic acid (50 + 30 + 4)
M128	Aqueous ammonium sulfate solutions (1.1-3.48 mol dm^3)
M129	Aqueous solutions of NaCl, NaBr, NaI, Na_2SO_4, $Na_2S_2O_3$, and $NaNO_3$
M130	Acetonitrile, methanol?? and their mixture in 1 + 1 ratio
M131	6.4% sodium dodecyl sulfate - 10% Triton X-100 - acetic acid sodium acetate buffer (pH 4) (5 + 8 + 3)
M132	Methanol - ethanol (7 + 3)
M133	Acetonitrile - benzene (69 + 31)
M134	Nine single- and 62 multicomponent solvent systems
M135	Aqueous salt solutions (0.2 M) and KCl - pyridine (100 + 5)
M136	Methanol - conc. HCl - water (8 + 1 + 1, 7 + 1 + 2), dioxane - 2-propanol - conc. HCl - water (7 + 7 + 5 + 8)
M137	HCl - H_3PO_4 - water (10 + 1 + 9)
M138	Aqueous solutions of NaCl, KCl, NH_4Cl, $CaCl_2$, $SrCl_2$, and $BaCl_2$
M139	Acetone - 3 N HCl (99 +)
M140	Buffer solutions (conc. ratio of acid to salt, 1:2)
M141	0.1 M HSCN in methyl ethyl ketone
M142	Glacial acetic acid - pyridine - 6 N HCl - 2,5-hexandione (120 + 9 + 30 + 1.5, *v/v*); upper layer of a well shaken mixture of butanol, 3 N HCl, and 2,5-hexandione

Table 5 (continued)

M143	Aqueous acetic acid solutions
M144	Salicylhydroxamic acid - isopropanol - 1 M HCl (0.153 g + 99 mL + 1 mL), salicylhydroxamic acid - isopropanol - *n*-butanol - ethanol - ethyl methyl ketone - 1 M HCl (0.153 g + 25 mL + 25 mL + 20 mL + 20 mL + 10 mL)
M145	1.02 M H_3PO_4
M146	0.01 M EDTA
M147	Alcoholic, acidic and alkaline solutions of salicylic acids at different concentrations
M148	Methanol - ether - 8 M HNO_3 (10 + 10 + 5, 10 + 10 + 1), 1-butanol - 10 M HNO_3 (1 + 1, 3 + 1, 5 + 1, 10, 1)
M149	7.5–10 % HCl in water or methyl ethyl ketone; 3–4 M LiCl in 1 N HCl
M150	Methanol - 5 N HCl (2 + 1); acetone - 1 N HCl (1 + 1)
M151	0.02–2.0 M H_2SO_4?? solutions; 0.01–1.0 M $(NH_4)_2SO_4$ solutions in 0.1 M H_2SO_4
M152	Mixed solutions (1.0 M in formic acid and 0.001–1.0 M in HCl)
M153	Binary and ternary mixtures of aqueous organic and mineral acids in different ratios
M154	Binary mixtures of 3 N HCl and methanol, ethanol, *n*-propanol or *n*-butanol (1 + 10)
M155	Mixed solutions of $(NH_4)_2SO_4$ and H_2SO_4, the concn of free H_2SO_4 being kept constant at 0.025 M
M156	Aqueous solutions of various inorganic salts
M157	Mineral and carboxylic acids at various concentrations
M158	6.0 M HCl - acetic acid (1 + 1, 1 + 3, 1 + 19)
M159	Mixed organic solvent systems containing HCl or HNO_3
M160	0.1–0.2 M tetraoctylamine solution in cyclohexane equilibrated with 7.2 M $LiNO_3$ solution
M161	Mixed aqueous NaCl - acetone solutions
M162	Mixtures of aqueous methanol (1, 6 and 11.2 M) and HCl in different ratios
M163	Mixtures of dimethylsulfoxide and HNO_3 (3, 6, and 12 M)
M164	Tetrahydrofuran - paraldehyde - conc. HNO_3 (20 + 70 + 10); 0.5 M triphosphine oxide in paraldehyde - conc. HNO_3 (1 + 1)
M165	*t*-Butyl alcohol - acetone (1 + 9), acetone methyl isobutyl ketone (3 + 2), methanol - methyl isobutyl ketone (1 + 8)
M166	Acetone - conc. HCl - water (85 + 8 + 7)
M167	Hexane - benzene - acetic acid (4 + 1 + 2), benzene - dioxane - formic acid (12 + 6 + 1), hexane - benzene - dioxane - formic acid (40 + 10 + 20 + 107), acetone - 0.1 M HCl (1 + 1), isopropanol - ethanol - 0.1 M HCl (3 + 1 + 1), ethyl acetate - ethanol - 1 M HCl (3 + 2 + 2)
M168	Aqueous CH_3COOH pH 2.0–2.5
M169	Ethanol - 1% NaOH solution (8 + 3), ethanol - 1% NaOH solution (2 + 1)
M170	Ethanol - 1% NaOH (2 + 1), ethanol - 1% NaOH (8 + 3), methanol - 1% NaOH (3 + 2)
M171	Aqueous solutions of HCl and HNO_3; 1 M HNO_3 - 1 M $NaNO_3$ (1 + 1); 0.1 M arsenic acid; 10% tartaric acid
M172	Aqueous phosphoric acid solutions (0.01, 0.1, 1 and 2 M)
M173	3 M Tributyl phosphate in HNO_3 - *iso*-octane (2 + 8); tetrahydrofuran - paraldehyde - HNO_3 (2 + 7 + 1); 0.3 M triphenylphosphine oxide in paraldehyde - HNO_3 (9 + 1), di-*iso*-propyl ether - tetrahydrofuran - HNO_3 (10 + 6 + 1)
M174	HNO_3 - methanol mixtures

Table 5 (continued)

M175	HNO_3 - dimethylsulfoxide (6 + 11); HCl - dimethylsulfoxide (6 + 4), HNO_3 - water (1 + 1)
M176	6 M HCl - MeOH (1 + 5); 8 M HCl
M177	Butanol - ethyl acetate - acetic acid - water (6 + 4 + 3 + 5, 8 + 4 + 3 + 5)
M178	Dimethylsulfoxide - HCl or HNO_3 systems
M179	Butanol - acetic acid - ethyl alcohol - acetone - water (6 + 1 + 3 + 4 + 1); isopropanol - acetic acid - acetone (13 + 1 + 7)
M180	Isobutanol - acetone - 0.2 M H_2SO_4 (4 + 3 + 1), tri-*n*-butylphosphate - acetone - 1 M HNO_3 (2 + 4 + 1), 1 M ammonium acetate - 1 M aqueous ammonia (2 + 1); 0.3 M $NaNO_2$, 0.5–2?? M aqueous ammonia
M181	Aqueous solutions of HCl (1–5 M), LiCl (1–9 M), $MgCl_2$ (2.5 M), $CaCl_2$ (2.5 M), and saturated NaCl
M182	Aqueous H_2SO_4 solutions
M183	Aqueous sodium chloride solutions
M184	Mixtures of aqueous ammonium nitrate and aqueous ammonia; 0.5 M ethanolamine + 0.5 M 2-hydroxyethyl ammonium nitrate, 2-aminoethylammonium nitrate (0.5–10 M)
M185	5% aqueous ammonia - ethanol - Me_2CO - HOAc in various ratios
M186	HCl or HNO_3 - 70% Me_2CO (1 + 1)
M187	Succinic acid - water - EtOH - aqueous ammonia
M188	Acetone - 6 M HCl (9 + 1); acetone - 4 M HCl - acetylacetone (45 + 3 + 2); butanol - 2 M HCl - acetylacetone (25 + 5 + 1); ethanol - 3 M HCl (9 + 1)
M189	Ethanol - acetone - acetic acid (7 + 5 + 2); ethanol - acetone - acetic acid (4 + 5 + 2)
M190	NaOH and HCl solutions in various concentrations
M191	*n*-Butanol, 3 M HCl (saturated), isobutanol, 3 M HCl (saturated), *iso*-propanol - 3 M HCl (7 + 3), glacial acetic acid - dry pyridine - conc. HCl (4 + 3 + 1)
M192	EtOH - Me_2CO - HOAc (10 + 15 + 3 and 18 + 15 + 5)
M193	1 M HBr - 1 M KBr (1 + 2)
M194	Glycine iminodiacetic acid, nitrilotriacetic acid, EDTA
M195	Acetone and ethyl methyl ketone in H_2SO_4
M196	H_2SO_4 and H_2SO_4 - $(NH_4)_2SO_4$ systems
M197	Mixtures of 5% aqueous ammonia, EtOH, acetone, and AcOH
M198	Mixtures of 5% aqueous ammonia - EtOH - Me_2CO - HOAc
M199	Et_2O - bis(2-ethylhexyl)phosphate - HNO_3 (100 + 3 + 2)
M200	(*iso*-Pr)$_2$O - THF - HNO_3 (1 + 3 + 1), Et_2O - THF - bis(2-ethylhexyl)phosphate - HNO_3 (100 + 15 + 3 + 6)
M201	0.2 M Trioctylamine and tetraoctylammonium chloride solutions in toluene
M202	Diethyl ether - bis-(2-ethylhexyl)phosphate - HNO_3 and diisopropyl ether - THF - HNO_3 mixtures
M203	*n*-Butanol - water - acetic acid - HCl (35 + 5 + 9 + 1)
M204	Benzene - ethyl acetate - acetic acid - HCl (60 + 30 + 10 + 0.5); benzene - ethyl acetate - acetic acid - HCl (60 + 30 + 10 + 1)
M205	Diethyl ether - bis(2-ethylhexyl)phosphate - HNO_3 (100 + 3 + 2); diisopropyl ether - tetrahydrofuran - HNO_3 (25 + 20 + 1), diethyl ether - bis-(2-ethylhexyl)phosphate - HNO_3 (50 + 2 + 1)
M206	1.0–2.0 M $NaNO_3$
M207	Aqueous acetic acid (0.1–3.0 M) and mixtures of acetic acid and ammonium acetate solutions
M208	*n*-Butyl acetate - conc. HCl (100 + 1.5)

Table 5 (continued)

M209	Polar and nonpolar solvents
M210	Me_2SO - HCl (1–6 M) (1 + 9, 3 + 7, 5 + 5, 7 + 3, and 9 + 1, *v/v*)
M211	Diethyl ether - bis(2-ethylhexyl)phosphate - HNO_3 (100 + 1 + 3.5), Et_2O - THF - bis(2-ethylhexyl)phosphate - KNO_3 (10 + 15 + 1 + 3.5)
M212	Ten aqueous and mixed solvent systems
M213	Mixture of short-chain alcohols and/or acetone with strong or weak acids
M214	Seventeen solvent mixtures
M215	5 M HCl with different concentrations of hydrogen peroxide
M216	Mixtures of Me_2CO, HCl, and water in various ratios
M217	Different concentrations of HCl and aqueous chloride solutions of Li, Mg, Na, Ca, Sr, and Ac
M218	Et_2CO - bis(2-ethylhexyl)phosphate - HNO_3 - Et_2CO - tetrahydrofuran, THF - bis(2-ethylhexyl)phosphate - HNO_3, and (*iso*-Pr)$_2$CO - THF - HNO_3
M219	HOAc - HCl
M220	Me_2CO - EtOAc - C_6H_6, (7 + 1 + 3).
M221	*iso*-Pr_2O - THF - conc. HNO_3 - H_2O (100 + 70 + 4.21 + 3.45)
M222	Aqueous HCl
M223	Polar solvent systems
M224	Water, aqueous solutions of NH_3, KCl, NaF, KNO_3, K_2SO_4, $KClO_4$ - Na_2CO_3, and K_3PO_4 at different molar concentrations
M225	Distilled water, aqueous sodium chloride (0.1–1%)
M226	1.0 M acetic acid and mixtures of 0.1 M acetic acid and ammonium acetate (pH 4.7, 5.7, 6.5 and 6.7)
M227	HNO_3 (0.01–1.0 M), DMF - 0.1 M HNO_3 (4 + 6), DMF - 0.1 M HNO_3 (6 + 4)
M228	0.1 M ammonium oxalate, DMSO - 1M HCl (1 + 9)
M229	Binary solvent systems
M230	3 or 5 M HCl containing $NaClO_4$
M231	Aqueous and aqueous - organic binary mixtures in various ratios
M232	Bu_3PO_4 - MeCOEt, EtOAc and HNO_3
M233	Dil. HNO_3
M234	Aqueous HCl
M235	Isopropanol - ethyl acetate - DMF - acetic acid - water (10 + 6 + 1 + 1 + 2), *iso*-propanol - ethyl acetate - DMF - acetic acid - water (60 + 30 + 3 + 5 + 10)
M236	10^{-3}-1.0 M HNO_3, dimethylformamide - 0.1 M HNO_3 (1 + 0, 4 + 1, and 1 + 4).
M237	Butanol - ethyl acetate - acetic acid (4 + 1 + 1) and ethyl acetate - formic acid - water - pyridine (3 + 1 + 1 + 0.5)
M238	0.05 M H_2SO_4 - methanol or acetone (1 + 0, 4 + 1, 3 + 2, or 2 + 3 *v/v*)
M239	Oxalic acid - oxalate systems
M240	Mixtures containing ether, THF, bis(2-ethylhexyl)phosphate, and HNO_3 in different ratios
M241	Me_2CO - HCl - water (45 + 2 + 3) and BuOH - HCl - water (45 + 4 + 6)
M242	Monotetradecyl phosphate (P 538), ethyl acetate, and HNO_3
M243	6 M HCl - acetylacetone - 9 M H_2SO_4 (60 + 2 + 1)
M244	Demineralized water, mixtures of sodium formate and formic acid solutions in different ratios
M245	MeOH - 6N HNO_3 - acetylacetone (4 + 3 + 1)
M246	0.5 M H_2SO_4 - acetone or methanol (1 + 0, 4 + 1, 3 + 2, and 2 + 3)

es and a subsequent increase in the number of publications on metal ions up to 1987 is, however, noticeable (curves I and II). After 1987 the trend was reversed, *i.e.* the number of publications on metal ions decreased and the number of publications on metal complexes has increased, with the exception of 1994. The TLC of anions (curve III) has gen-

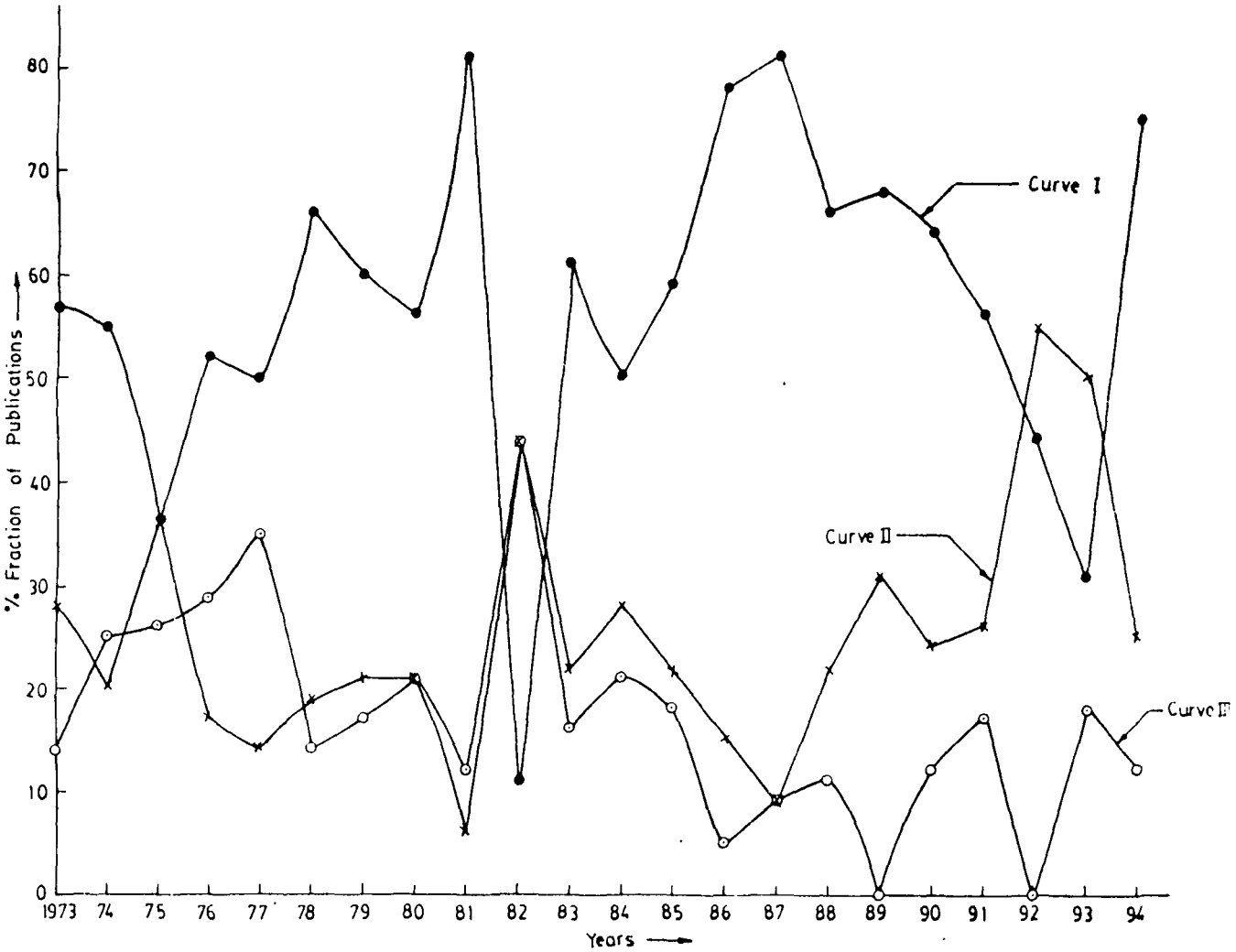


Figure 1

Relative proportions of publications devoted to the analysis of different inorganic species in each year during the period 1973–1994. Curve I, metals and metal ions; Curve II, metal complexes; Curve III, metal anions.

erally been neglected, the number of publications in this field being significantly lower than that for metals and metal ions and for metal complexes.

It is apparent from **Figure 2** that the percentage of publications on metal ions plus metal complexes per year, calculated as:

$$\text{Perc.} = \frac{\text{No. of publications on metal ions + metal complexes} \times 100}{\text{No. of publications on metals + metal complexes + anions}}$$

falls in the range 59 to 76.

The total number of papers published on the TLC of inorganic species (*i.e.* cations, anions, and metal complexes) during 1973–1990 fluctuated between 9 and 28, showing no definite pattern. Between 1990 and 1994 the number of publications has gradually decreased.

The number of publications appearing during 1973–1994 in important chromatographic and analytical journals is shown in **Figure 3**. Investigators have preferred to publish their papers in journals dealing exclusively with chromatography rather than more general analytically oriented journals.

3 Future Prospects

It is apparent from the literature that most of the papers on inorganic TLC originate from research laboratories of the less developed countries, probably because of the lack of

more sophisticated instrumentation. Although TLC and HPTLC have maintained a prominent position in Europe in the recent past, their growth in the USA has been limited.

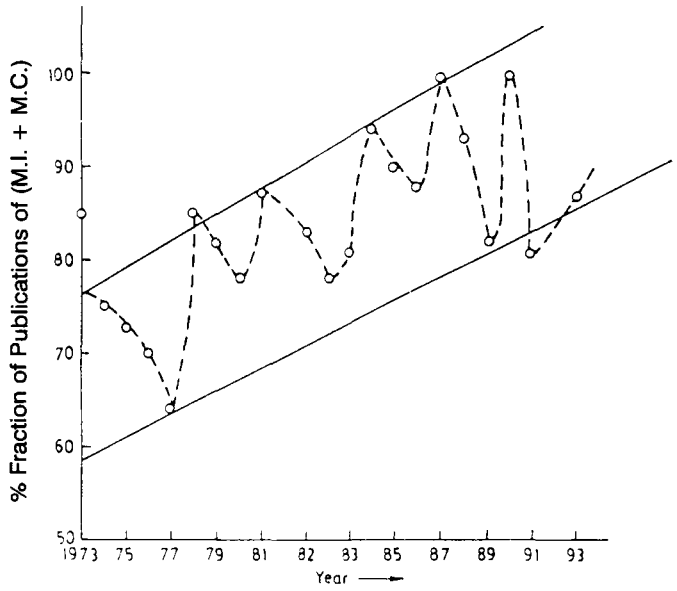


Figure 2

The variation in the number of publications on metal ions (M.I.) and metal complexes (M.C.) during the period 1973–1993.

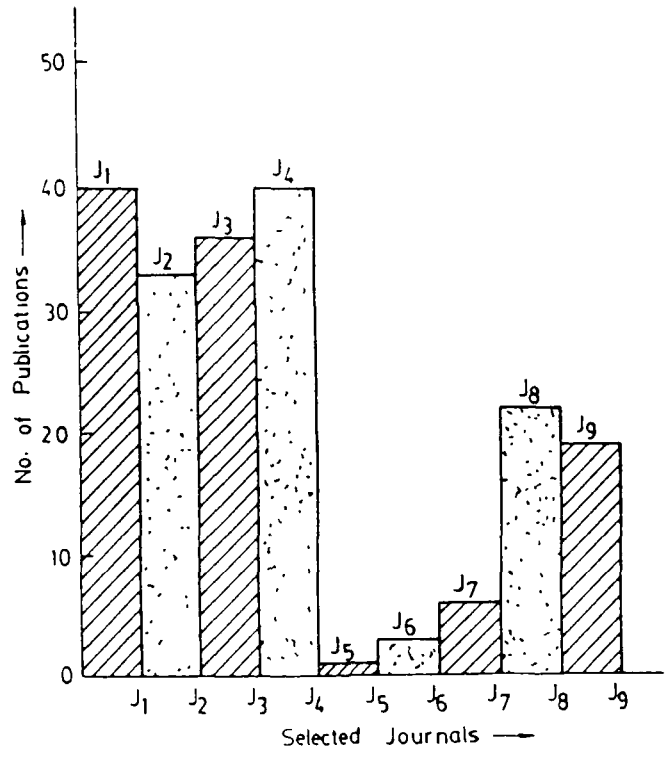


Figure 3

Number of publications on inorganic TLC appearing selected journals during 1973–1994. J_1, J. Chromatogr.; J_2, J. Liq. Chromatogr.; J_3, J. Planar Chromatogr.; J_4, Chromatographia; J_5, J. Chromatogr. Sci.; J_6, Microchim. Acta; J_7, Bunseki Kagaku; J_8, Fresenius J. Anal. Chem.; J_9, Zh. Anal. Khim.

Interest in the USA is, however, now increasing as a result of the development of computer- and microprocessor-based instrumental TLC for application-oriented research in several fields. The Journal of Planar Chromatography - Modern TLC, launched in 1988 has published many important current research publications in TLC and HPTLC and it seems that TLC and HPTLC will enjoy popularity as an analytical tool for qualitative identification and quantitative analysis of pharmaceutical, environmental, agrochemical, forensic, cosmetic, and food samples. Future emphasis will be on improved layer quality, automation of sample application, greater use of instrumental densitometry, on-line coupling of TLC with other sensitive techniques, direct scanning of radioactive isotopes, better approaches in method development and application of detection reagents, and improved instrumentation with increased automation for forced-flow systems. According to the latest selective review on the literature of TLC and paper chromatography (PC) (November 25, 1991 to November 1, 1993) by *Sherma* approximately 10% of papers discuss inorganic analysis compared with almost nine times more publications on the analysis of organic species. In our opinion new TLC, HPTLC, and forced-flow layer methods will be used in the future for application-oriented analysis of inorganic ions in real samples, *e.g.* food, natural waters, wastewater, textiles, soil, and biological, geological, and pharmaceutical samples, *etc.*

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Review Paper

TLC In Organic Environmental Analysis

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In this report an attempt has been made to present the work carried out during last twenty-four years on the application of thin layer chromatography (TLC) in the analysis of organic environmental pollutants. The literature search wascarried out by manual screening of the Chemical Abstracts selected for Environmental Analytical Chemistry. In most cases the matrices from which the pollutants have been isolated and chromatographed include air, water, waste water, soil/sediment and industrial wastes.

Most of the reviews appeared in literature so far are specific in nature reporting the work carried out either on one pollutant or pollutants in a single matrix. The reviews covering the literature on TLC as used in combination with other analytical techniques are also available. Though some interesting reviews in Chinese, Russian, Japanese and German languages are reported in literature but these reviews are neither frequently available nor easily understandable to many readers. Therefore the necessity of a review dealing with environmental aspects of thin layer chromatographic analysis is felt.

The present review is aimed to examine the developments of TLC procedures in the fields of environmental analysis. The period reviewed is 1970-94 and selective references have been reported to confine to the space limit. It appears that TLC being a cost effective and more efficient than low pressure column chromatography is destined to play an even greater role in our "high tech" society in future.

I. Books/Book Chapters :

Some of the most important Books/Book chapters dealing with TLC of organic environmental toxicants include : **Paper and Thin Layer Chromatographic Analysis of Environmental Toxicants**[1] ; **Methods for the Identification of Trace Amount of Pesticides and Products of their Transformation in Environmental Samples**[2] ; **Advances in Thin-Layer Chromatography :Clinical and Environmental Applications** [3] ; **Determination of Chlorinated Agro-chemicals by Thin-Layer Chromatography : Chlordane Determination** [4] ; **Quantitative TLC of Cholinesterase Inhibiting Pesticides Residues by Reflective Scanning** [5] ; **Chromatographic Analysis of the Environment** [6] ; **Environmental Analysis using Chromatography Interfaced with Atomic Spectroscopy** [7] **and Hand book of Thin-Layer Chromatography : edited by J. Sherma and B. Fried** [8]. **Below is given a brief outline about the contents discussed in the above mentioned books.**

An analytical scheme for detection of pesticides and their reaction products in water, soil, air etc. including thin-layer chromatography in which various sorbents, mobile solvents are used and a gas - liquid chromatography on columns of various polarity, is suggested. The use of the scheme is illustrated by identification of photolysis products of dithio-and thio-phosphates and s-triazone pesticides[2]. α Chlordan (I) and 14 other organo chlorine pesticides were detected in water by TLC using silica gel as the carrier, a hexane - ethyl acetate solution as the developing agent and a 5% O-toluidine alcoholic solution as colouring agent [4]. Comparison were made between the use of indoxyl acetate and acetyl thiocholine as substrates for horse serum cholinesterase for quantitative TLC of cholinesterase inhibiting pesticide residues, 2,4-Dichloroindophenol was used as the redox dye, and reagents were applied to TLC plates by spraying and dipping. Carbofuran and its metabolites and phorate metabolites were detected. Low nanogram amounts of cholinesterase - inhibiting residues were detected by combination of the enzyme inhibition technique and reflectance scanning of visualized spots [5]. It is a comprehensive laboratory handbook [8] divided into two parts, the first part discusses the theory, practice and instrumentation of TLC whereas the second part describes applications of TLC to a variety of compounds. Some of the chapters of this book are excellent collection of data on environmental applications of TLC to phenolic materials, pesticide residues, PAHs and other substances.

II. Reviews :

The following reviews discussing the role of TLC in organic environmental analysis have appeared in recent past.

In-situ Fluorescence Spectroscopy of Pesticides and other Organic Pollutants : Fluorometric analysis of organic pollutants, especially pesticides, in solution and on paper and thin-layer chromatograms is discussed[9].

The Application of Liquid Phase and Thin Film Chromatography to the Analysis of Organic Water Polluting Agents : This review covers the detection of hydrocarbons, polycyclic aromatic hydrocarbons, (PAHs), phenols, detergents, pesticides and other organic compounds in water by TLC and liquid phase chromatography. Ninty four references are cited[10].

Chromatographic Needs of the Environ-mental Chemist : Analysis in routine monitoring and research project is discussed [11].

Instrumental Thin - Layer chromatography : Advantages of application of instrumental TLC in food analysis are discussed. Examples of and conditions for quantitative determination of caffeine in foods and DES in veal and calves urine as well as ascorbic acid in fruit juices are detailed[12].

Chromatographic - Atomic Absorption Analysis and its Application : The combination of atomic absorption detection with gas, gel and liquid chromatography and its use in the analysis of multicomponent samples such as biological, environmental, and fuel are discussed. It contains 47 references [13].

Quantitative Thin-Layer Chromatography of Foods and Beverages : Twenty references have been cited to cover the application of TLC for analysis of alfatoxins, diethyl stilbestrol, caffeine, sugars and their components in food and beverages [14].

Thin-Layer Chromatography for Determi-nation of Herbicide Residues in Soil : It is a brief review on the determination of herbicides in soil samples. It contains 17 references[15].

Determination of a Pattern of Polycyclic Aromatic Hydrocarbons (PAHs) in Food and Environmental Samples. Clean up, TLC in situ Fluorescence Characterization : This review with seven references includes determination of PAH in food and environmental monitoring, sample clean-up, TLC on cellulose acetate layer, in-situ fluorescence determination and fluorescence interferences[16].

The Use of Radio Thin Layer Chromatography in Pesticide Environmental Studies : The use of radio-TLC in the analysis of pesticides in environmental samples is summarized in a brief review containing 4 references. Both analytical TLC and preparative TLC are covered[17].

Combination of Thin Layer Chromatography and Infra-red Spectroscopy in the Analysis of Water, Wastewater and Sludge ; An Introduction : A review with 25 references discussing the preparation of numerous substance groups of non-polar to polar character occuring in water, wastewater and sludges or sediments for IR spectroscopy by using TLC with selected mobile phase is reported. The substance (5-100 (ug) required for IR spectroscopy is isolated on silica gel layers through multistage chromatography. In addition to substance groups from the aquatic environment, metabolites from the biochemical degradation of technological products (e.g. detergents) as well as of single compounds (e.g. surfactants) are included in the examples and the results obtained with the combination of TLC and IR spectroscopy are summarized[18].

Chromatography in Environmental Analysis : The special volumes of Journal of Chromatography were published to cover all techniques of chromatography including TLC for environmental analysis[19].

A review with 98 references on environmental analysis of amines, phenylenediamines and diphenylamines by TLC, GC, HPLC and super critical fluid chromatography[20].

A review containing TLC analysis of pesticides, phenols, organometallic compounds, polynuclear aromatic hydrocarbons etc. in water with 15 references is reported[21].

A review on the determination of plant protecting agents and pesticides in drinking water by means of HPTLC is presented with 50 references[22].

III. Research Papers :

Thin Layer Chromatographic data obtained on commercially available silica gel coated films and glass fiber sheets are compared with those achieved on hand coated silica gel glass plates for a number of drugs of toxicological interest. Running rates, relative running rates, solvent mobilities and general characteristics of the different media for TLC are reported[23].

The results of separation and identification of triazine herbicides (simazine, atrazine, terbulethyl azine, ametryme, metoprotryne desmetryme, terbutryme, prometryme, terbutylation) achieved by thin - layer chromatography and gas chromatography were compared[24]. Two samples of water were extracted with 80, 50 and 30 ml CH_2Cl_2 and evaporated in vacuum at low temperature. One residue in 0.5 ml solvent was examined by TLC, and the second residue in 0.25 ml solvent was injected into the chromatographic column containing Ucon 2000. The limit of detection with gas liquid chromatography and TLC were 500 ppb and 25 ppb respectively. The extraction of triazines from 1 litre water at pH 7 was quantitated at concentration level below 500 ppb. However, the extraction method needs to be improved for quantities $\simeq$ 50 ppb. Chromato graphic methods for the determination of residuce of s-triazines [25] and residual amounts of prefix and casaron [26] in water samples are developed.

A TLC method is described for the identification and qualitative detection in drinking water of triasalkofen BMB and tetra alkofen BPE antioxidants and dibauryl thiodipropionate (DLTDP) synergist contained in plastics formulations for articles in the water supply system. The method was used to detect the migration of the additives from polypropylene articles into drinking water[27].

Detection limits, semiquantitative determination and threshold values were determined for DDT and its metabolites by performing TLC on five different sorption layer materials and developed with hexane. Seven visualization agents were used to achieve the lowest

possible detection limit. The best results (detection limit < 0.1μg.) were obtained on silufol UV 254 layer using $AgNO_3$ - NH_4OH detection reagent (UV visualization). The possibility of applying the proposed method for water pollution by DDT is explored[28].

Reversed phase TLC was used to detect chloroalkane carboxylic acids and chlorophenoxyalkane carboxylic acids as well as their derivatives (esters with C_{1-5} alcohols) in water[29]. The acids were identified on the basis of the chromatographic methods and different types of intermolecular interactions, which improve the reliability of the identification.

New one - dimensional and two dimensional HPLC methods were developed for the analysis of drinking water samples containing PAHs less than 50 /ug / L and more than 50 /ug/L concentration levels respectively. Chromatogram developed in the usual way with a 9:1:1 acetonitrile - dichloromethane - water mixture was visually compared with that of a standard solution in order to achieve semiquantitative detection of PAHs [30].

A rapid one - dimensional HPTLC method developed for detecting PAHs in drinking water required 15-20 minutes whereas a slower two - dimensional TLC procedure (development time 3 h.) was used to differentiate between contaminated and almost uncontaminated waters. The chromatogram is produced on a RP-18 TLC plate with a concentration zone using an acetonitrile - dichloromethane - water mixture in a volume ratio 9 : 1 : 1 as a developing solvent. Evaluation is done by visual fluorescence and comparison of samples with standard solutions. The borderline between contaminated and uncontaminated waters was set at 50 μg/L [31].

Combination of TLC and infrared spectroscopy for identification of organochlorine pesticides in their determination in water is reported [32]. TLC on silica gel plates in a hexane - Et_2O — HOAc (50 : 50 : 2) system and on alumina plates in a hexane system followed by IR spectroscopy of evaporated C_5H_5 extracts placed in KBr tablets permits the identification of pesticides extracted from H_2O by IR spectra of DDT are presented as an example.

Use of TLC for analysis of nonionic surfactants and determination of their trace amounts in waste waters and petroleum is proposed [33]. Ascending TLC on silica gel with $CHCl_3$ -EtOH (100:2.5) as the mobile phase and Tragendorff's reagent as the detector were used for identifying polyethylene glycol and OP 10 in oil well waters and petroleum. The decrease in R_F values with increasing molecular weight of the analysis could be used to approximate determination of the molecular weight. Satisfactory separations were also obtained with Al_2O_3 or silchrom S stationary phase.

Carbamate pesticides e.g. carbofuran and carbaryl, and organophosphorous (OP) pesticides, e.g. phorate sulfoxide were detected in water samples by silica gel TLC. The solvent systems for the OP pesticides was hexane - Me_2CO - $CHCl_3$ (60:30:5) and for the carbamate pesticides was cyclohexane - EtOAc (4:3). TLC spots were scanned by densitometry. Average recoveries for these pesticides ranged from 94.8% carbaryl to 84.8% for the phorate organic anolog[34].

Two methods were developed for the determination of both linear and branched long - chain alkyl benzenes in complex environmental samples. One of the methods includes the isolation of a pure alkylbenzene fraction from total lipid extracts using argentation TLC and subsequent analysis by high resolution gas chromatography. Another method involving direct analysis of hydrocarbon fractions by high - resolution gas chromatography / TLC / GC technique is better, suited for routine analysis of environmental samples containing only one of the two alkylbenzene types (eg. wastes, detergents). For the more complex alkyl benzene assemblages sometimes encounter in waste-affected sedimentary deposits, the GC/MS has the advantage of being able to discriminate between linear and branched varieties based on differences in the respective fragmentation pattern's [35].

Preparation of environmental samples for the analysis of PAHs by TLC is discussed [36]. For particulate samples, solvent extraction using a soxhlet apparatus or ultrasonication was preferable to sublimation and liquid-liquid distribution between hexane and DMSO followed by silica gel column chromatography was the preferred method for sample clean-up. Using this procedure, PAHs (Anthracene, fluoranthene, benzo (a) anthracene, perylene, pyrene and coronene) were determined quantitatively in urban air particulates, diesel engine exhaust particulates, laboratory ventilator dusts, household dusts, river water and tea samples. The PAHs were identified by coincidence of retention between the sample and standards in the same chromatographic system and by adequate agreement with standards for their normalized emission response ratios. The two-point calibration method was used for quantitation. Good agreement for the concentration of PAHs in the air particulate and diesel particulate extracts with published data using gas chromatography - mass spectrometry and HPLC was found.

A thin layer chromatographic method for detecting formaldehyde in environmental samples, (such as soil, water, air) agricultural products and biological samples is based on the extraction of formaldehyde with dimedone followed by TLC of the derivative on silufol plates [37]. The method allowed the detection of 0.004 ±0.001 mg formaldehyde in water, 0.003 ±0.001 mg formaldehyde/m^3 in air and 0.6 – 1.2 μg formaldehyde/ml.

Thirty - three organophosphorous pesticides were identified and detected in various samples (food, soil, water etc.) containing other pesticides by TLC on silufol. The detection and quantification involved the use of ammonia and bromine vapors, choline esterase and indoxyl acetate.

Detection limits of 10^{-10}, 10^{-9} g were achieved [38] (Russ.).

Analytical procedure to classify organic pollutants in natural waters and environment is proposed[39]. The organic pollutants were classified into four types using TLC as- alkanes, PAHs, chlorinated organic compounds, phthalates and organic alcohols. Quantity of each type of organic compounds was determined by gas chromatography - mass spectrometry with fused silica capillary column. The technique was practised in study of organic pollutants in sediments, sea water, ground water in the area of Rhode Island USA (Ch).

Application of TLC - flame ionization detection to the analysis for natural lipids and pollutant compounds in sea water, sediments microalgae and marine animals are presented. The method combines good sensitivity, ease of use and the ability to resolve most of the compound classes of interest in marine samples[40].

A new and sensitive analytical technique has been developed for the simultaneous determination of six aromatic amines[41]. It is based on the differential migration of colored derivatives formed by the reaction of the diazotized amines with 6-amino-1-naphthol-3- sulfonic acid on a silica gel plate. The concentration of analyte evaluated by color comparison or by spectrophotometry under the influence of a temperature gradient. The method is highly reproducible and has been applied to the determination of amines in environmental samples with standard deviations of 4.6-7.31.

A HPTLC method for the detection of diacetoneketogluconic acid in water samples was reported by A. Eisenbeiss et al. Silica gel coated TLC plates were developed with chloroform - methanol (8:2) and chloroform - methanol - acetic acid (80:20:2) and the acid was detected by immersing TLC plate in 4-methoxybenzaldehyde solution and heating at 130° C for 2 min. For quantitative determination fluorodensitometry at 366 nm was used[42].

A method for determination of 24 pesticides in water by HPTLC using automated multiple development technique is reported. Two 20 - step elution gradients based on dichloromethane and on ter-butyl methyl ether were tested. Using HPTLC silica gel layer of 100 mm and the running distance increments as 1 mm, both sensitivity and speed of the procedure were increased. Densitometric determination was performed by absorbance detection at 200, 220, 240, 260, 280 and 300 nm (multiwavelength)[43].

PAHs were isolated from industiral exhaust fumes and characterized by two - dimensional thin - layer chromatography (Al_2O_3 - acetyl cellulose 2:1 plates with hexane - toluene 9:1 and MeOH-Et_2 O-H_2O 4:4:1 as mobile phase). Retention time values in gas chromatography, excitation and emission fluorescence spectra in solution and on thin layer chromatograms and by UV and mass spectra (both excitation and emission) measured directly on thin layer chromatograms and in solutions was observed for some compounds. The R_f and retention time values were correlated with the molecular weight of the hydrocarbons[44].

PAHs were separated by two - dimensional thin - layer chromatography and detected by fluorescence spectroscopy. The class to which a compound in a spot on the chromatogram belongs was identified by mass spectroscopy[45]. The method was used to determine PAHs in urban air.

An analytical method allowing detection of aflatoxins in a complex matrix was developed[46]. An apparatus that quantitates fluorescent compounds on thin - layer chromatographic plates was fabricated. Laser excitation source produces a detection limit of 10 pg for four aflatoxins. Aflatoxin B_1 was found at levels of $\leq$ 17 ppb in solid samples collected from the air at a plant which produces refuse derived fuel.

HPTLC was used to determine atmospheric concentrations of the active ingredients in pharmaceutical preparations, e.g. levonorgestiel, ethymylestradiol and quinine sulfate in air. The eluted spots were detected quantitatively by UV or visible absorbance measurements[47].

A TLC method developed for the identification of azaarenes in the organic content of airborne particulate matter includes the chromatography of eight azaarenes on cellulose layer developed with DMF-water mixtures (1:9, 1:4, 7:13, 1:1, 13:7). After drying visualization under UV 254 nm and exposure to trifluoroacetic acid vapour followed by visualization under UV [48].

HPTLC on silica gel with seven solvent systems was used for the analysis of chrysoidine dyes and densitometric determination (436 nm) of chrysoidine Y and R in air samples [49].

Non-volatile hydrocarbons in a marine sediment extracts were detected by TLC (using $CHCl_3$ extracts, SiO_2 plate and hexane solvent) with precision approaching obtained by gas chromatography [50]. Saturated hydrocarbons unsaturated hydrocarbons, and total non - volatile hydrocarbons were also detected with precision 8-12%, relative standard deviation. Elemental sulfur, phthalate esters and traces of chlorinated hydrocarbons did not interfere. This method is useful for oil spill source identification.

Thin layer chromatographic method for the determination of polycyclic aromatic and aliphatic hydrocarbons in airborne particulate matter is developed[51]. The cyclohexane solution fraction of airborne particulates was separated by TLC into three polycyclic aromatic hydrocarbon fractions and one aliphatic hydrocarbon fraction suitable for gas - liquid chromatographic analysis. The benzopyrene and benzofluoranthene isomers were completely resolved.

Spectrophotometric and chromatographic methods for the determination of the presence of organophosrous pesticides in objects of animal and plant origin are discussed[52] (Russ.).

Some applications of flame ionization detection TLC in the leather industry are described [53]. The method is simple and can be used for the rapid detection of the products used, fats extractable from leather and the changes in the composition of fattiquoring baths and of spews (Fr.), and 10 to 100 gng for HPTLC plates with alkaline sodium nitroprusside potassium hexa cyanoferrate (III) chromogenic reagent.

Gas chromatography (GC) with packed and capillary columns, high - performance liquid chromatography (HPLC) and TLC were used to characterize various commercially available mixtures of polychlorinated terphenyls (PCTS) in environmental samples[54]. UV absorption and mass spectrometry data were also collected and the behaviour of PCTs upon perchlorination to the terta decachloroterphenyls was examined. Using GC, the PCT content of a number of paper and sewage sludge samples was detected.

A simple, quick and accurate method was developed for isolation and detection of organic compounds such as pesticide residues in environmental materials[55]. A sample (e.g. sludge extracted with CH_2Cl_2) was applied on a silica gel TLC plate predried at 105°C for 30 min. and developed with CCl_4 until the solvent front moved to 10 cm. The scraped material from the silica layer between 6 and 35 mm from the original line was extracted with Me_2CO, and the extract was analyzed by high performance gas chromatography [column 5%, OV-17 on chromosorb W (60-80 mesh); column temperature 200°C, carrier gas N_2 at 50 ml/min.]. This method gave a high recovery rate and sharp separation for heptachlor, aldrin, heptachloroepoxide, dieldrin and endrin added to sludge. The TLC method also gave satisfactory recovery of anthracene, fluoranthene and benzo(a) pyrine but not of naphthalene (Japanese).

Some chlorinated organic pesticides such as aldrin (I), lindane (II) and DDT (III) were detected by TLC on silica gel. Petroleum ether -CCl_4 (1:1) and cyclohexane - $CHCl_3$ (4:1) were used as the solvents systems. The detection threshold values were 0.1 µg for I and II, and 0.5 µg for (III) [56] (Albanian).

Chloridazon, bentazon, atrazine, simazine, prometryn and propazine are detected in milk by TLC on silica gel H, G or LSL with a toluene - Me_2CO (85:15) or benzene - $CHCl_3$ - EtOAc (2:2:1) mixture as a mobile phase and visualization with 0-toliudine and KI solutions. The sensitivity of the method was 0.02-0.05 µg/g, the recovery of herbicides from spiked milk samples collected from 46 dairy farms was 90%. About 28.3% milk samples were found to contain residues of chloridazon, prometryn, atrazine or simazine [57] (Czech).

An applicable TLC technique for field screening polychlorinted biphenyls (PCBs) was developed. Quantitative analysis by TLC densitometry can be done in laboratory (or in a field van). A densitometer is needed for quantitative work by TLC and semi-quantitative results can be obtained by visual comparisons. Confirmation can be made by visualization with silver halide on TLC plate. Dehalogenation with Na-biphenyl, chlorination with $SbCl_5$ or mass spectral confirmation can also be used. Quantitative analysis of the derivatized samples is possible [58].

Pesticides were extracted from apples, grapes, cucumbers and pears with acetonitrile, re-extracted with $CHCl_3$, applied to a column of Na_2SO_4 10, florisil 10, celite 8, and activated carbon, eluted with $CHCl_3$ and determined by TLC using 0.1% bromophenol blue for qualitative detection and Dragendroff reagent for semiquantitative determination. Recovery of Gardona and Rubigan was 90-100%, Torque 80-100% and Afugan 70-80%[59] (Bulg).

A method developed for the quantitative determination of pyrazole derivatives in biosphere substances[60], consists of extraction of a mixture of derivatives from samples with an organic solvent, concentration of extracts by evaporation, removal of co-extractive substances by redistribution in an organic solvent - acid system, neutralizing of acid and alkalizing the solution, re-extracting the mixture of the derivatives from an aqueous phase with an organic solvent, repeated concentration TLC in a system of organic solvents and detection of stained spots of the separated derivatives. The selectivity and sensitivity are increased by extraction with $CHCl_3$; using 5 N HCl in purification; re-extracting the derivatives with $CHCl_3$ at pH 8-9; chromatography of the mixture in a hexane-acetone system (5:3) ; and by detection with an I_2-starch reagent after n-halogenation with prior UV irradiation of plates. For separation of the derivatives from soil samples the extraction is carried out with acetone with subsequent evaporation of the extract until dry (Russ.).

Tetrafluoroterephthalodinitrile was determined semiquantitatively by HPTLC and TLC[61]. Amongst solvent systems (MeOH, $CHCl_3$ and CH_2Cl_2), CH_2Cl_2 gives best results. Comparison was made of four glass backed silica gel plates incorporating a fluorescent inhibitor used without activation. The R_f values determined under vapor saturation conditions were in the range 0.33 - 0.66. The detection limits were 50 to 200 ng for conventional plates and 10 to 100 ng for HPTLC plates with alkaline sodium nitroprusside potassium hexacyanoferrate (III) chromogenic reagent.

Conculsion :

We have reviewed the literature on the application of TLC technique for screening and determining the concentration of toxic chemicals and organic pollutants in water, air and sediments. It has been observed that extensive study has

been done in identification and determination of PAHs organophosphorous and chlorinated pesticides in water and air matrices. Future efforts should be directed to develop sensitive and rapid TLC/HPTLC methods for determining PCBs and other chlorinated toxic compounds at trace levels. It is needless to prove that in the past five years GC has been the most popular technique with highest number of publications whereas TLC/HPTLC has not received as much attention as required in spite of its advantageous features like easy handling, low cost investment, reasonable sensitivity and versatility. It is proposed that TLC should find more and more applications for preliminary routine screening of a variety of environmental samples.

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